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EVIDENCE BEARING ON THE SOLVATE THEORY OF SOLUTION.*

BY

HARRY C. JONES.

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This paper has been written in response to a request from the Editor of the JOURNAL OF THE FRANKLIN INSTITUTE, to summarize for *this journal* the experimental evidence obtained in my laboratory, bearing upon the solvate theory of solution as it originated here about fourteen years ago.]

THE solvate theory of solution was proposed from this laboratory in 1900 [1] to account for certain apparently abnormal freezing-point lowerings produced by certain electrolytes when dissolved in water. These had been observed by Jones and Ota,[2] and Jones and Knight,[3] and a large number of such cases were brought to light by Jones and Chambers,[4] and by Chambers and Frazer,[5] working with Jones.

Jones and Getman [6] then took up this problem systematically, and found that this abnormally great lowering of the freezing-point of water produced by dissolved substances in concentrated

* Communicated by the author.

[1] *Amer. Chem. Journ.*, 23, 89 (1900).

[2] *Ibid.*, 22, 5 (1899).

[3] *Ibid.*, 22, 110 (1899).

[4] *Ibid.*, 23, 89 (1900).

[5] *Ibid.*, 23, 512 (1900).

[6] *Zeit. phys. Chem.*, 46, 244 (1903). *Phys. Rev.*, 14, 146 (1904).

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solution was a more or less general phenomenon. It was manifested to the greatest extent by those substances which crystallize from aqueous solutions with the largest amounts of water of crystallization. Indeed, the magnitude of the freezing-point lowering was nearly a linear function of the water of crystallization.

This suggested that there is probably some connection between the two sets of phenomena. The question was, what is this connection? Water of crystallization is essentially water of hydration out of solution. A salt brings with it out of solution a certain amount of water, which it can hold in more or less stable equilibrium under the conditions under which it ordinarily exists. Other things being equal, that salt which can hold the largest amount of water in combination as water of crystallization out of solution, would be the salt which, in solution, would combine with the largest amount of water. Indeed, it is difficult, on *a priori* grounds, to see why a salt should combine with water when leaving the solution, and hold this water with the stability with which water of crystallization is held; and not combine with water when in solution,—*i.e.*, when in the presence of a large amount of water.

These were the facts at that time available, and this the line of thought which led me, in 1900, to suggest, as a tentative explanation of the apparently abnormally large freezing-point lowerings produced especially by concentrated solutions of most substances, what was then called the *hydrate theory of solution.* The idea was that when substances are dissolved in water they combine with more or less of it; the amount depending upon the nature of the dissolved substance. If this suggestion were true, if dissolved substances do combine with a part of the water present, thus removing it from the field of action so far as solvent is concerned, then we could account satisfactorily for the large freezing-point lowerings. There being less solvent present than we supposed, the lowering of its freezing-point by the dissolved substance would be greater than we would expect; since freezing-point lowering is proportional to the ratio between the number of parts of the dissolved substance and number of parts of the solvent.

Further, this explanation would also account for the fact that the freezing-point lowerings become more and more abnormally great as the solution becomes more and more concentrated.

The more concentrated the solution the larger the total amount of water held in combination by the dissolved substance. Hence, the smaller amount of water remaining free and, therefore, playing the role of solvent. Consequently, its freezing-point would be lowered more and more.

This explanation would, then, account for all of the facts observed; the question is, Is it true? There might be other explanations that would account for these facts as well as, or better than, this one. Is there any evidence that this is the correct explanation?

The aim of this paper is to bring together the various lines of experimental evidence bearing upon this question, which have come to light as the result of fourteen years of continuous work in my laboratory on this problem. In this work there have taken part more than *forty* investigators, and each of these has worked on his problem from *one to five years*, making a total of from *75 to 100 years' work for one man.* The more important of this evidence will now be briefly discussed.

I. RELATION BETWEEN LOWERING OF FREEZING-POINT AND WATER OF CRYSTALLIZATION.

The work of Jones and Getman [7] brought out a relation between lowering of freezing-point and water of crystallization. They worked with a large number of chlorides, bromides, iodides, and nitrates, measuring the freezing-point lowerings produced by solutions of these substances of known concentrations; and, from the lowerings found experimentally, calculated the corresponding molecular lowerings. They then compared with one another the molecular lowerings produced by the various chlorides. Similarly, the molecular lowerings produced by the various bromides and iodides. Finally, the molecular lowerings produced by a large number of nitrates were compared. The result was the discovery of the relation between the magnitude of the freezing-point lowering produced by the different substances, and the amounts of water with which these substances crystallized under the same conditions from aqueous solution.

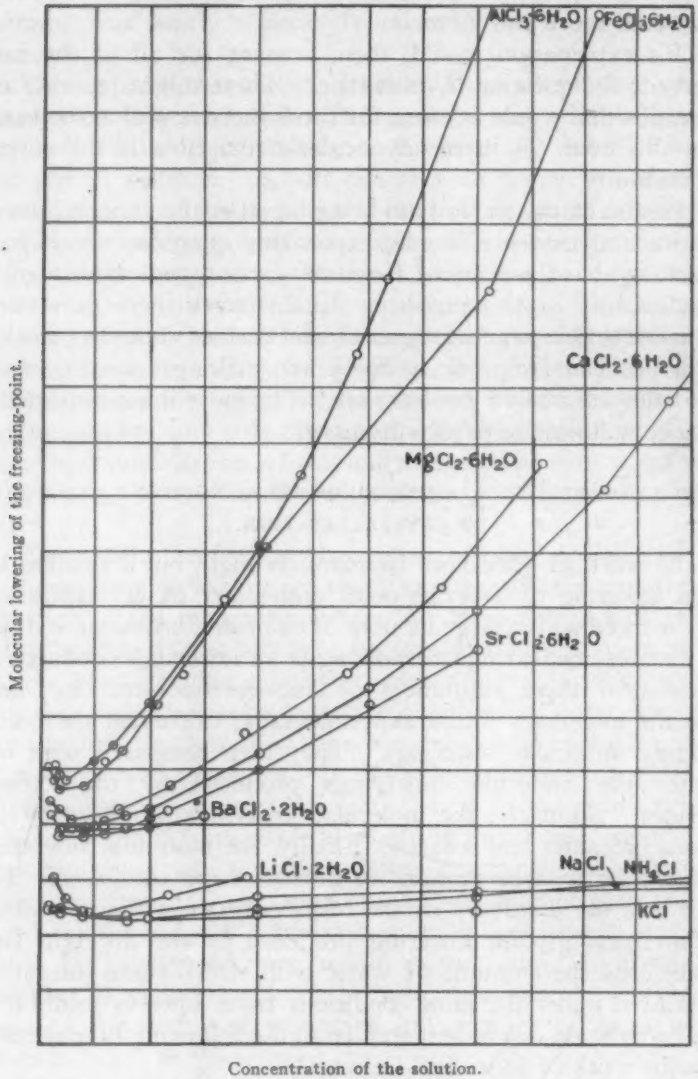
This relation can be best seen from the following figures taken from the work of Jones and Getman.[8]

[7] *Zeit. phys. Chem.*, 46, 244 (1903); *Phys. Rev.*, 18, 146 (1904); *Amer. Chem. Jour.*, 31, 303 (1904); Carneg. Inst. of Washington, Publication No. 60.

[8] *Zeit. phys. Chem.*, 49, 433 (1904); *Journ. Chem. Phys.*, 3, 478 (1905).

The freezing-point lowerings produced by the following chlorides were measured: sodium, potassium, ammonium, lithium,

FIG. 1.



barium, strontium, calcium, magnesium, iron, and aluminium. From the freezing-point lowerings found experimentally, the

molecular lowerings were calculated for a number of concentrations. The molecular lowerings as ordinates were plotted against the molecular lowerings as ordinates were plotted against the concentrations as abscissæ. The curves are shown in Fig. 1.

The chlorides of sodium, potassium, and ammonium, which crystallize without water, fall at the bottom of the sheet. Then comes the chloride of lithium with two molecules of water. Barium chloride, with two molecules of water, is considerably above the chloride of lithium, but barium chloride is a ternary electrolyte, yielding three ions, while lithium chloride is binary,

The chlorides of calcium, strontium, and magnesium, each crystallizing with six molecules of water, give curves which fall nearly together, and are much higher on the curve sheet than the chlorides which crystallize without water.

We finally come to the quarternary chlorides of aluminium and iron, which crystallize with six molecules of water each. These give much greater molecular lowerings than the ternary chlorides with the same amount of water of crystallization. The molecular lowerings of the freezing-point, then, produced by the various chlorides, are a function of the amounts of water with which these salts crystallize. But molecular lowering of the freezing-point is an expression of the amount of water which the salt holds in combination in solution. Therefore, the amount of water with which the chlorides are in combination in solution, is a function of the amount which the chloride is capable of bringing with it out of solution as water of crystallization.

The bromides of cadmium, potassium, sodium, lithium, barium, strontium, calcium, and magnesium were studied in an exactly similar manner, and the results plotted as curves. These substances fall in the same order on the curve sheet as the amounts of water with which they crystallize.

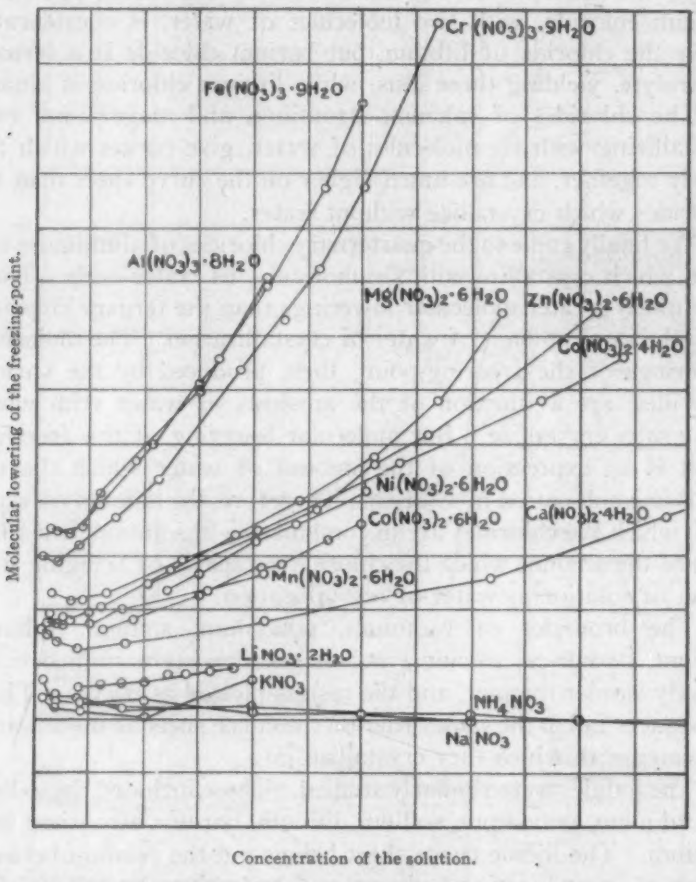
The iodides were similarly studied. These included the iodides of cadmium, potassium, sodium, lithium, barium, strontium, and calcium. The iodide curve-sheet brings out the relation between water of crystallization and water of hydration, just as satisfactorily as the chloride and the bromide sheet.

The nitrates as a class are very soluble salts. For this reason a large number of these substances were studied, and the results obtained plotted as curves. The nitrate sheet (Fig. 2) includes the nitrates of sodium, ammonium, potassium, lithium, calcium,

manganese, cobalt, nickel, cadmium, zinc, magnesium, iron, chromium, and aluminium.

The nitrates of sodium, ammonium, and potassium, which crystallize without water, fall at the bottom of the sheet. The last point in the curve for potassium nitrate is an error in plotting the

FIG. 2.



curve. This curve practically coincides with the curves for sodium and ammonium nitrates. Lithium nitrate, with two molecules of water of crystallization, falls a little above the curves for the other alkaline nitrates. Calcium nitrate is especially interesting. It crystallizes with four molecules of water, and falls below the

curves for the salts with six molecules of water. It will be recalled that calcium chloride, like the chlorides of strontium and magnesium, crystallizes with six molecules of water, and its freezing-point curve is practically coincident with those of the other alkaline earth chlorides. The nitrate of calcium, crystallizing with four molecules of water, would, in terms of the relation we are now studying, be expected to fall below the nitrates with six molecules of water, and such is the fact. This compound alone adds special interest to the nitrate sheet.

The nitrates of manganese, cobalt, nickel, zinc, and magnesium, each crystallizing with six molecules of water, give freezing-point curves which fall very close together, and which are higher on the sheet, showing greater lowering of the freezing-point than the curve for calcium nitrate.

Finally, we come to the quarternary chlorides of iron, aluminium, and chromium. These crystallize with eight and nine molecules of water. They lower the freezing-point of water more than any other known nitrates. Indeed, their freezing-point lowering is from *four to five times as great* as would be calculated on the assumption that there is no combination between the solvent and the dissolved substance. The same is true of the chlorides of these elements.

We have compared above the salts of the same acid with different metals. Relations of interest and importance manifest themselves between the salts of the same metal with different acids.

Chlorides, bromides, iodides, and nitrates crystallizing without water all give a molecular lowering of between 3 and 4. This increases very slightly with increase in concentration. Lithium chloride, with two molecules of water of crystallization, gives about the same freezing-point lowering as lithium nitrate with two molecules of water, and less lowering than lithium bromide or iodide, with three molecules of water each. The bromide and iodide give about the same freezing-point lowering.

Sodium bromide and iodide each crystallizes with two molecules of water, and they produce very nearly the same lowering of the freezing-point.

Barium chloride, bromide, and iodide all crystallize with two molecules of water. Since barium chloride is only slightly soluble, the comparison must be limited to dilute solutions. Here all

three salts show about the same lowering of the freezing-point of water. In the more concentrated solutions the iodide shows greater lowering than the bromide. If we compare the chlorides, bromides, and iodides of the alkaline earths, they all crystallize with six molecules of water, and they produce lowerings of the freezing-point of the same order of magnitude. The bromides give slightly greater lowerings than the chlorides, and the iodides than the bromides.

The nitrates give just about the same lowerings as the corresponding chlorides, and, therefore, slightly less than the bromides and iodides.

The nitrates of iron and aluminium, with nine and eight molecules of water of crystallization, give greater lowerings than the corresponding chlorides which crystallize with six molecules of water each.

Thus, *the relation between water of crystallization and lowering of freezing-point comes out on every hand, whether we compare the salts of a given acid with different metals, or the salts of the same metal with different acids.*

A study of all of the data obtained by Jones and Getman seemed to justify the conclusion that "*Those substances which crystallize with the largest number of molecules of water of crystallization, give the greatest molecular lowering of the freezing-point of water in concentrated solutions.*"

The number of compounds studied by Jones and Getman was sufficiently large to show that the above relation is a general one. It is obvious that this relation is a fundamental one. Those substances which combine with the largest amounts of water out of solution, water of crystallization, would be the ones which would form the more complex hydrates in solution. These would be the compounds which would produce the greatest lowering of the freezing-point of water, and, consequently, the greatest molecular lowering; since the water which is combined with the dissolved substance as water of hydration is removed from the field of action, so far as solvent is concerned. Having established the relation between lowering of freezing-point and water of crystallization, Jones and Getman calculated the composition of the hydrates formed by a number of substances at various dilutions. To do this, it was necessary to know the molecular lowering of the freezing-point at the dilution in question, the molecular lower-

ing calculated from the dissociation at the same dilution; and the amount of water present in a given volume of the solution.

Jones and Getman [9] found that the composition of the hydrates formed by a given substance at various dilutions, increased with the dilution, as would be expected from the law of mass action. They found also that the total amount of water combined with the dissolved substances increased with the concentration of the solution, and plotted curves expressing the relation between total amount of water in combination and the concentrations of the solutions. These curves were found to be perfectly regular for all of the substances investigated. This is also what would be expected from the law of mass action. This was all regarded as good preliminary evidence, at least, that there is combination between the dissolved substance and the water.

2. RELATION BETWEEN WATER OF CRYSTALLIZATION AND TEMPERATURE OF CRYSTALLIZATION.

Another consequence of the hydrate theory of solution is the following: It is a general fact that rise in temperature decreases the complexity of complexes. Hydrates are no exception to this relation. It is a very simple matter to remove from a saturated solution all of the water except that with which the salt crystallizes. It is only necessary to maintain it at its boiling-point for a sufficient length of time. The hydrate in solution under such conditions must have approximately the same composition as the salt with its water of crystallization. This same salt was shown from our work to form hydrates in more dilute solutions and at lower temperature, which are many times more complex than the salt with crystal water. Thus, calcium chloride crystallizes with six molecules of water of crystallization. It was found that a molecule of calcium chloride in more dilute solution and at lower temperatures can combine with at least thirty molecules of water.[10] These facts all show that the hydrates are relatively unstable, breaking down with rise in temperature.

Since a salt holds less water in combination with it the higher the temperature to which the solution is heated, it would seem to

[9] *Zeit. phys. Chem.*, 49, 447 (1904).

[10] Either the molecule or the resulting ions can combine with this amount of water.

follow that a salt should bring with it out of solution less and less water the higher the temperature at which it crystallizes. In a word, a salt should have less and less water of crystallization the higher the temperature at which it crystallizes.

That this was in general true was a well-known fact. We were, however, surprised on examining the literature to find how general this relation is, and what wide differences in water of crystallization manifested themselves for such a large number of substances.

A few examples taken from the work of Jones and Bassett [11] well illustrate this point. Take the chlorides of magnesium, iron, and manganese, and the nitrates of nickel and cobalt. The number of molecules of water of crystallization and the temperatures of crystallization are given:

Salt with number of molecules of water of crystallization	Temperature of crystallization
$MgCl_2.6H_2O$	$-10°$ to $-12°$
$MgCl_2.12H_2O$	$+20°$
$MgCl_2.10H_2O$	above $+20°$
$MgCl_2.8H_2O$	Higher temperatures.
$FeCl_2.6H_2O$	$-16°$ to $+20°$
$FeCl_2.3\frac{1}{2}H_2O$	$+20°$
$FeCl_2.2\frac{1}{2}H_2O$	$+40°$ to $+60°$
$FeCl_2.2H_2O$	$+60°$ to $+80°$
$FeCl_2.0H_2O$	$+80°$ and above.
$MnCl_2.12H_2O$	$-48°$
$MnCl_2.11H_2O$	$-21°$ to $-37°$
$MnCl_2.6H_2O$	$-21°$
$MnCl_2.4H_2O$	$+15°$
$MnCl_2.2H_2O$	$+20°$
$Ni(NO_3)_2.9H_2O$	$-27°$
$Ni(NO_3)_2.6H_2O$	$-16°$
$Ni(NO_3)_2.3H_2O$	$+58°$ and higher.
$CO(NO_3)_2.9H_2O$	$-29°$ to $-22°$
$CO(NO_3)_2.6H_2O$	$-22°$ to $+56°$
$CO(NO_3)_2.3H_2O$	$+56°$ to $+91°$
$Cu(NO_3)_2.9H_2O$	$-20°$ to $-24°$
$Cu(NO_3)_2.6H_2O$	$0°$ to $-10°$
$Cu(NO_3)_2.3H_2O$	Ordinary temperatures.

[11] *Zeit. phys. Chem.*, 52, 1231 (1905).

Calcium chloride crystallizes with the following amounts of water as the temperature of crystallization is lower and lower:

Salt with number of molecules of water of crystallization	Temperature of crystallization
$CaCl_2.6H_2O$; $CaCl_2.4H_2O$; $CaCl_2.2H_2O$; $CaCl_2.H_2O$;	
$Mg(NO_3)_2.9H_2O$	$-17°$.
$Mg(NO_3)_2.6H_2O$	$+18°$
$Mg(NO_3)_2.2H_2O$	Higher temperatures.
$MnSO_4.7H_2O$	$0°$ to $+6°$
$MnSO_4.5H_2O$	$+15°$ to $+20°$
$MnSO_4.4H_2O$	$+25°$ to $+31°$
$MnSO_4.3H_2O$	
$AlBr_3.15H_2O$	$-10°$ to $-18°$
$AlBr_3.6H_2O$	At ordinary temperature.
$AlI_3.15H_2O$	$-18°$
$AlI_3.6H_2O$	At ordinary temperature.

A large number of examples were found illustrating this same point, but those given above will suffice to show how regularly water of crystallization decreases with rise in temperature. This relation seems to be a perfectly general one. So far as is known to the writer, there is not a single exception to this general relation.

Jones and Bassett carried out some preliminary experiments, which made it probable that some well-known compounds can be made to crystallize with still larger amounts of water than had hitherto been supposed to be possible, by crystallizing them at very low temperatures. The general relation between water of crystallization and temperature of crystallization is, then, just what would be expected from the solvate theory of solution. The higher the temperature the simpler the hydrates existing in aqueous solution. The higher the temperature of crystallization the simpler the hydrates which separate as water of crystallization when the salt crystallizes out of the solution. This is all in keeping with the hydrate theory of solution, and can be regarded as evidence for it. Indeed, it is difficult to see how hydrates (salts with water of crystallization) could separate out of solution if they did not exist in solution. It is almost inconceivable that a salt would combine with water on leaving the solution as crystals, and hold that water in fairly stable combination as water of crystallization; and would not combine with even more water when in solution in that solvent,—*i.e.*, when in the presence of a large excess of water. The law of mass action would almost force us to this conclusion.

However this may be, the direct line of evidence referred to above is the point upon which it is desired here to lay stress.

3. MINIMA IN THE BOILING-POINT CURVES.

An examination of Figs. 1 and 2 will show that practically all of the curves pass through a well-defined minimum. The minima in the freezing-point curves are for very dilute solutions. Let us see just what these minima mean. With increasing dilution the molecular lowerings of the freezing-point increase, due to increasing dissociation. This causes the curves to rise as the dilution is increased. With increasing concentration the curves would continue to fall, did not hydration take place. Hydration removes more and more water from the field of action as solvent, and, consequently, the remaining smaller and smaller amount of water with increasing concentration has its freezing-point lowered more and more. Therefore, the molecular lowering increases more and more the greater the concentration of the solution. This would tend to make the freezing-point curves rise with the concentration. The minimum in a freezing-point curve is, therefore, the point where these two conditions just equalize one another. Starting with the most concentrated solution and proceeding towards the more dilute, we have the curve approaching the abscissæ, due to the total amount of combined water becoming less and less as the dilution becomes greater and greater. With increasing dilution, however, the dissociation becomes greater and greater, and this would cause the freezing-point curve to rise. Where these two opposite influences are just equal to one another in effect, we have the minimum in the curve. On the more dilute side of the minimum, the effect of increasing dissociation more than overcomes the opposite effect of decreasing hydration and the curve rises. On the more concentrated side of the minimum, the effect of increasing amount of combined water more than overcomes the opposite effect of decreasing dissociation, and the curve rises here also; whence the minimum. With this explanation in mind of the nature of the minimum in the freezing-point curves, we can now understand another line of evidence bearing on the solvate theory.

Jones and Getman,[12] having furnished the evidence already discussed in connection with the relation between lowering of freezing-point and water of crystallization; and having calculated the composition of the hydrates formed by a large number of

[12] *Amer. Chem. Journ.*, 32, 338 (1904).

substances at various dilutions in water as the solvent, turned to various solvents to see what evidence could be obtained as to whether solvents other than water combined with substances dissolved in them. They studied certain salts in ethyl alcohol, not measuring their lowering of the freezing-point, since this would be impossible on account of the low temperature at which alcohol freezes; but the rise in the boiling-point. Boiling-point curves were obtained in which the molecular rise in the boiling-point were plotted against concentrations of the solutions. *Minima* were also *found in the boiling-point curves,* but these were at *greater concentrations* than the minima in the freezing-point curves. Let us see just what this means. The minima in the freezing-point curves were the points at which decreasing hydration with increasing dilution, tending to make the curve fall, was just offset by increasing dissociation which made the curve rise.

Just so it is with the boiling-point curves. Here, however, where the temperature was higher the hydration was less; since, as we have seen, hydrates are more and more unstable the higher the temperature to which they are heated. It would, therefore, require at the boiling-point of the solution, greater concentration to secure the necessary hydration, in order that this effect might overcome the opposite effect of dissociation. We should, therefore, expect to find the minimum in the boiling-point curves at a greater concentration than in the freezing-point curves, and such is the fact.

This was brought out by the work of Jones and Getman already referred to; and also by that of Jones and McMaster[13] along the same general line.

These and other investigations in this laboratory showed that solvents other than water do combine with at least certain substances dissolved in them, and that we have not simply hydration in aqueous solutions, but alcoholation in the alcohols. Other work, which will be referred to later, has shown that glycerol also combines with more or less of the dissolved substance, and that we have glycerolation as well as alcoholation. Similar work in acetone shows that this solvent combines with more or less of the dissolved substance, as we shall see. We thus have not simply a theory of hydration in aqueous solutions, but of *solvation* in solvents in general. *The hydrate theory thus becomes the solvate theory of solution.*

[13] *Amer. Chem. Journ.*, 35, 316 (1906).

The important point in the present connection is that the minimum in the boiling-point curves, being at greater concentration than in the freezing-point curve, is in keeping with the solvate theory. Indeed, it could have been predicted from the theory before a single fact was established experimentally, and is, therefore, regarded as evidence in favor of the theory.

4. HYDRATING POWER AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY.

The conductivities of solutions of electrolytes are a function of two things: The number of the ions and the velocities with which they move. The conductivities of solutions increase in general, with rise in temperature. This must, therefore, be due either to an increase in the number of ions present, or to an increase in the velocity of the ions. It has been shown beyond question that rise in temperature does not increase the number of ions present. Indeed, the effect of rising temperature is to diminish the number of ions present—to diminish the dissociation.

The increase in conductivity with rise in temperature must, then, be due to an increase in the velocity with which the ions move. This can be brought about in a number of ways. The ions may move faster with rise in temperature, due to a diminution in the viscosity of the solvent which always takes place as the temperature rises. The magnitude of this change in viscosity with rising temperature has been worked out in this laboratory not only for water, but for a large number of nonaqueous solvents.[14] It has been found that the increase in conductivity with rise in temperature, is due largely to a breaking down of the complex hydrates as the temperature rises. Starting with this fact, certain relations of interest and importance between the temperature coefficients of conductivity and the magnitude of the hydration have been discovered.[15] These relations were first pointed out from the theory of solvation, and then verified by the experimental facts.

That the complex hydrates break down with rise in temperature has been shown beyond question. The higher the temperature the less complex the hydrate existing around the ion. The less complex the hydrate attached to the ion, the less the mass of the ion, and the less its resistance when moving through the

[14] See Publications of the Carnegie Institution of Washington, Nos. 80 and 180.
[15] *Amer. Chem. Journ.*, 35, 445 (1906).

solvent. If this decreasing complexity of the hydrate about the ion has any pronounced effect in determining the magnitude of the temperature coefficients of conductivity, then the following deductions from the solvate theory were made, as necessary conclusions from this theory, before a single experimental fact was examined to see whether the conclusions were verified.

It would seem reasonable to suppose that the more complex the hydrate about any ion, the greater would be the change in the complexity of the hydrate as the temperature is raised. The larger the number of molecules of water combined with an ion, the larger the number that could, and probably would be split off with rise in temperature. In a word, from the solvate theory *those ions with the greatest hydrating power would be the ones that would be expected to have the greatest temperature coefficients of conductivity;* since the temperature coefficients of conductivity are determined largely by the decrease in the complexity of the hydrate with rise in temperature. This is one conclusion from the solvate theory in connection with the temperature coefficients of conductivity.

If different ions have approximately equal hydrating power, we should expect the change in the complexity of these hydrates to be of about the same order of magnitude. Therefore, *ions with approximately equal hydrating power, should have temperature coefficients of conductivity of the same order of magnitude.* This conclusion can also be tested by the experimental facts.

The hydrates existing in solution have been shown by Jones and his co-workers to be more complex the more dilute the solution. The hydrates being more complex in the more dilute solutions, the change in the composition of the hydrates with rise in temperature would be greater in the more dilute solutions. Therefore, we should expect that the *temperature coefficients of conductivity would be greater the more dilute the solution studied.* This conclusion, like the two foregoing, can be tested by the results of experiment.

One other conclusion is of interest and importance: The higher the temperature the more unstable the hydrate. We should therefore expect the breaking down of the complex hydrates into simpler hydrates, to take place more rapidly at the higher temperatures. The result would be that *the temperature coefficients of conductivity would be larger the higher the temperature.* This conclusion can also be tested by the experimental facts.

The following data are taken from the work of this laboratory, published by the Carnegie Institution of Washington; Monograph No. 170, page 77:

TABLE I.

Substances with slight hydrating power.	Temperature coefficients in conductivity units. 25° to 35°		50° to 65°	
	v=8.v=1024		v=8.v=1024	
Sodium chloride	2.00	2.46	2.27	2.82
Sodium bromide	1.89	...	2.18	2.79
Sodium iodide	2.12	2.54	2.33	3.14
Sodium nitrate	2.04	2.45	2.02	2.67
Sodium chlorate	1.77	2.22	2.15	2.90
Potassium chloride	2.39	2.84	2.45	3.11
Potassium bromide	2.43	2.91	2.45	3.11
Potassium iodide	2.38	2.91	2.65	3.37
Potassium nitrate	2.08	2.16	2.31	2.83
Potassium chlorate	2.02	2.52	2.23	2.94
Potassium permanganate	2.04	2.31	2.29	2.23
Potassium sulphocyanate	2.20	2.56	2.34	...
Ammonium chloride	2.42	2.94	2.51	3.69
Ammonium bromide	2.32	2.86	2.58	3.11
Ammonium nitrate	2.17	2.50	2.33	3.04

TABLE II.

Substances with large hydrating power.	Temperature coefficients in conductivity units. 25° to 35°		50° to 65°	
	v=8.v=1024		v=8.v=1024	
Calcium chloride	3.49	4.85	...	...
Calcium bromide	3.73	5.00	4.03	6.03
Calcium nitrate	3.09	4.79	3.33	...
Strontium chloride	3.37	5.13	3.92	6.02
Strontium bromide	3.66	5.27	4.08	...
Strontium nitrate	2.76	4.86	3.58	...
Barium nitrate	3.09	4.74	3.34	...
Magnesium chloride	3.40	4.72	3.61	...
Magnesium bromide	3.55	4.44	4.08	...
Magnesium nitrate	3.10	4.78	3.57	...
Zinc nitrate	3.13	4.47	3.43	5.41
Manganous chloride	3.14	4.86	3.43	6.37
Nickel chloride	3.41	5.04	3.61	...
Nickel nitrate	3.21	4.58	...	...
Cobalt chloride	3.39	4.95	3.54	...
Cobalt bromide	3.32	4.96	3.75	...
Cobalt nitrate	3.20	4.67	3.05	...
Cupric nitrate	3.18	4.88	...	...
Aluminium chloride	4.57	8.64	5.16	12.49
Aluminium nitrate	4.19	7.86	4.87	11.65

These facts suffice to test the above conclusions from the hydrate theory. The compounds in Table I have slight hydrating power, as would be expected from the fact that they crystallize with little water of crystallization, or with no water at all. Those in Table II all crystallize with large amounts of water, although with different amounts of water. These substances are all strongly hydrated.

The substances in Table I have much smaller temperature coefficients of conductivity at all temperatures and dilutions than those in Table II. This is true even taking into account the fact that the substances in Table I are all binary electrolytes; while those in Table II are in general ternary; the chloride and nitrate of aluminium being quarternary electrolytes.

The second conclusion can also be tested by comparing Tables I and II. The substances in Table I all have slight hydrating power,—*i.e.*, they all have hydrating power of the same order of magnitude. Their temperature coefficients of conductivity are all of the same order of magnitude.

Those in Table II have very great hydrating power, yet all have hydrating power of approximately the same order of magnitude. This would be expected from the fact that most of these substances crystallize with six molecules of water. The temperature coefficients of conductivity of most of the substances in Table II are of the same order of magnitude. Aluminium chloride crystallizes with six molecules of water, and aluminium nitrate with eight. These are quarternary electrolytes and have, therefore, larger temperature coefficients of conductivity.

The third point, that temperature coefficients of conductivity are greater at the higher dilution, can also be tested by the above facts. A comparison of the temperature coefficients in both tables, —*i.e.*, for those substances which hydrate very little and those which hydrate largely,—will show the larger coefficients for the higher dilutions.

The fourth and last conclusion, that the temperature coefficients should be greater the higher the temperature, is also borne out by the experimental results.

To summarize the four conclusions from the solvate theory, which are substantiated by the experimental facts, we have:

1. The temperature coefficients of conductivity are larger the greater the hydrating power of the salt.

2. The temperature coefficients of conductivity for substances having approximately the same hydrating power are approximately the same.

3. The temperature coefficients of conductivity increase with the dilution of the solution, being greatest for those salts with large hydrating power.

4. The temperature coefficients of conductivity increase with the temperature; the increase being greatest for those substances with large hydrating power.

The conclusions from the solvate theory are thus confirmed by the facts at every point, so far as the temperature coefficients of conductivity are concerned. The number of these deductions is so large, and the confirmations so satisfactory and convincing, that this is regarded as very strong evidence in favor of the general correctness of the theory of solvation in solution. Without this theory it seems impossible to explain a single one of the above relations.

The following co-workers have investigated this phase of the problem: West,[16] Jacobson,[17] White,[18] Clover,[19] Wightman,[20] Hosford,[21] Winston,[22] Kreider,[23] Springer,[24] Howard,[25] Shaeffer,[26] and Smith.[27]

This work has all been published as a monograph,[28] by the Carnegie Institution of Washington.

5. DISSOCIATION AS MEASURED BY THE FREEZING-POINT METHOD AND BY THE CONDUCTIVITY METHOD.

The water that is combined with the molecules, or the ions resulting from the dissociation of the molecules, is removed from

[16] *Amer. Chem. Journ.*, 34, 357 (1905); 44, 508 (1910).
[17] *Ibid.*, 40, 355 (1908).
[18] *Ibid.*, 42, 520 (1909); 44, 135 (1910).
[19] *Ibid.*, 43, 187 (1910).
[20] *Ibid.*, 46, 56 (1911); 48, 320 (1912).
[21] *Ibid.*, 46, 240 (1911).
[22] *Ibid.*, 46, 368 (1911).
[23] Carnegie Institution of Washington, Publication No. 170.
[24] *Amer. Chem. Journ.*, 48, 411 (1912).
[25] *Ibid.*, 48, 501 (1912).
[26] *Ibid.*, 49, 207 (1913).
[27] *Ibid.*, 50, 1 (1913).
[28] Carnegie Institution of Washington, Publication No. 170.

the field of action so far as solvent is concerned. This, as we have seen, affects the freezing-point lowering directly. The lowering of the freezing-point of a solvent by a given amount of a dissolved substance, depends upon the ratio between the number of parts of the substance and solvent. The part of the liquid present not acting as solvent plays no part in the freezing-point lowering. Therefore, the freezing-point lowering shown is much greater than if there was no hydration; and greater, just in proportion to the amount of solvent combined with the substance as water of hydration.

If half of the water were combined as water of hydration, the freezing-point lowering of the remaining half would be just double what it would be if there were no hydration. If two-thirds of the water present were in a state of combination, the freezing-point lowering would be three times that of an unhydrated substance, and so on. The dissociation calculated from the abnormally great freezing-point lowering would, of course, be abnormally large. In a word, freezing-point lowering would be affected almost lineally by hydration.

The dissociation of electrolytes as measured by the conductivity method depends upon two factors, the number of the ions in a given volume of the solution and the velocities with which they move. The hydrated ions would move slower than the unhydrated, having a greater mass. The number of the ions would probably not be greatly affected by the hydration. It would seem, therefore, that hydration would have less effect on dissociation as measured by the conductivity method than as measured by the freezing-point method. We predicted, before trying a single experiment, that dissociation as measured by the freezing-point method would be greater than as measured by the conductivity method. Dr. J. N. Pearce [29] took up in my laboratory a fairly elaborate investigation of this point. He measured the dissociations of calcium, strontium, magnesium, and barium chlorides; the nitrates of calcium, strontium, magnesium, and barium; cobalt chloride and nitrate; copper chloride and nitrate; nickel nitrate; aluminium chloride; sodium bromide; hydrochloric, nitric, and sulphuric acids;—over as wide range of dilution as the freezing-point method could be used. The nature of the results obtained can be seen from the following data, taken from the paper by Jones and Pearce:

[29] *Amer. Chem. Journ.*, 38, 411 (1907).

Salt.	Concentration.	Dissociation from conductivity.	Dissociation from freezing-point lowering.
$CaCl_2$	0.01	89.67	90.61
	0.05	80.62	80.96
	0.10	74.35	76.35
$BaCl_2$	0.10	75.65	78.83
	0.05	80.09	85.19
	0.01	90.87	96.85
$MgCl_2$	0.01	73.61	87.68
	0.05	79.78	90.97
	0.01	90.90	97.10
$SrCl_2$	0.10	74.17	84.46
	0.05	78.08	82.65
	0.01	89.37	91.87
$Ba(NO_3)_2$	0.01	61.36	62.95
	0.05	70.47	75.18
	0.01	86.37	99.06
$Ni(NO_3)_2$	0.075	76.57	81.32
	0.05	79.83	83.72
	0.01	91.10	98.03
$Co(NO_3)_2$	0.01	76.48	85.48
	0.05	81.73	88.26
	0.01	92.40	98.65

Solutions much more concentrated than the above were also studied, but on account of the hydration it was impossible to determine their dissociation by the freezing-point method. Hence, the comparisons were made at the above dilutions.

An examination of the above data will show that the dissociation as measured by the freezing-point method is greater than as measured by conductivity. This was found almost invariably to be the case. The prediction from the solvate theory was thus fully confirmed by the experimentally established facts. This is regarded as evidence in favor of the theory from which the prediction was made.

One other point bearing upon the solvate theory of solution came out in this work of Pearce, which is interesting and probably important: The freezing-point data for the most concentrated solutions were used as the basis for calculating the composition of the hydrates present in the solutions. It was found that *the hydrating power of a salt is primarily a function of the cation.*

The relation in question is between the atomic volumes of the elements and their power to form hydrates. If the atomic volumes are plotted as ordinates and the atomic weights as abscissæ, we have the well-known atomic volume curve, which brings out a periodic relation. Potassium, rubidium, and cæsium fall at the highest maxima. Salts of these elements crystallize without water. Lithium and sodium also fall at maxima on this curve, but at much lower maxima. The salts of these elements crystallize with two and three molecules of water, and show in solution some hydrating power. The atomic volumes of lithium and sodium are smaller than those of potassium, rubidium, and cæsium.

At the minimum in the third division of the atomic volume curve we find strontium, iron, cobalt, nickel, and copper. Salts of these elements crystallize with large amounts of water, and these salts when in solution show large hydrating power. Aluminium with about half the atomic weight of iron, has a slightly larger atomic volume, falling at the second minimum of the curve. Its salts crystallize with eight and nine molecules of water, and show the very greatest hydrating power in solution.

Of the calcium group, barium has the largest atomic volume and the smallest hydrating power; strontium, with a larger atomic volume than calcium, has a smaller hydrating power than calcium; while magnesium has the smallest atomic volume of this group, and the greatest hydrating power. An examination of all the data available shows that the *hydrating power of the cation is an inverse function of its atomic volume.* The question arises, What does this mean? what is its physical significance? The smaller the ion, probably the greater the electrical density of the charge upon it. The power of the ion to combine with the solvent seems to be a function of the electrical density of the charge upon the ion.

6. HYDRATING POWER OF THE IONS AND THEIR VELOCITIES.

Another relation that was brought out by the work of Pearce, has proved useful in explaining certain apparent discrepancies which presented themselves in the relative velocities with which the ions move. It is well known that the velocities of the ions are an inverse function of their mass and probably, also, a function of their volumes. We should expect those ions with the

smallest atomic volumes to have the greatest velocities. We frequently find the opposite. Potassium, rubidium, and cæsium, with the exception of hydrogen and hydroxyl, have the highest velocities; while the elements of the iron and copper group, which have very small atomic volumes, have the smallest migration velocities.

If we study the two curves representing the relation between atomic volumes and atomic weights, and between migration velocities and atomic weights, it shows at once the cause of this apparent anomaly. It has been shown that those elements which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We see, then, that *those ions which have the smallest migration velocities have also the greatest hydrating power.*

A somewhat detailed comparison of the members of the different groups will bring out this idea more clearly.

The atomic volumes of potassium, rubidium, and cæsium increase rapidly with increasing atomic weights, and, as a rule, their salts crystallize without water. We should expect, then, the potassium ion to have the greatest migration velocity, and the cæsium ion to have the smallest. Experiments show that they have approximately the same migration velocities. Sodium and lithium, whose atomic volumes are less than half that of potassium, have migration velocities which are only about two-thirds that of potassium. It will be remembered that sodium and lithium form salts which may crystallize with two and three molecules of water, respectively. Hence, we may assume that the increase in volume of the sodium and lithium ions, due to the formation of a relatively large hydrate, decreases the velocity of those ions to a far greater extent than the slight hydration of the large potassium ion decreases the velocity of that ion.

The atomic volume of lithium is about one-half that of sodium, and the maximum amount of water with which lithium salts crystallize from solution is three molecules, whereas the maximum for sodium salts is two molecules. Since the ratio of 2 : 3 represents approximately the ratio of the hydrating power of the two ions in solution, we should expect the effect upon the velocity, of the greater increase in the volume of the small lithium ion, due to its hydration, to compensate somewhat for the smaller increase in the volume of the larger sodium ion. Experiment shows that the migration velocities are nearly equal.

The same relation holds for the metals of the alkaline earth group. The atomic volumes increase with increasing atomic weight. The migration velocities of the cations calcium and strontium, whose salts crystallize with six molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with two molecules of water, or water-free. On the other hand, the magnesium cation, which has one-half the atomic volume of the calcium ion, has nearly the same migration velocity, due to compensation between the atomic volumes and the hydration of the ions.

The calcium ion has a slightly greater atomic volume than sodium, yet, owing to its much greater hydrating power, its migration velocity is considerably less.

The cations of copper, cobalt, and nickel have nearly the same atomic volumes and the same hydrating power. We should expect them to have the same migration velocity, and such is the case.

The atomic volumes of the halogens, chlorine, bromine, and iodine, are approximately the same. If their ions are hydrated we should expect them to combine with the same amount of water, and, therefore, they should give migration velocities of the same order of magnitude. This has been found to be the case. The atomic volume of fluorine has not been determined, but from its position on the migration velocity curve we should infer that its atomic volume is smaller than that of the halogens, and that its ion possesses a considerable degree of hydrating power.

Further, it will be noted that the migration velocities of the halogens are almost identical with those of the alkalies standing next above them in order of atomic weights, whereas their atomic volumes are very much smaller. This leads us to believe that the compensation, which brings about an equalization of the migration velocities of the two groups, is due to the increase in volume of the alkali ions by hydration.

The silver ion alone of all the metallic elements for which satisfactory data can be found presents an exception. It has a small atomic volume, and its salts crystallize from solution without water. We should expect it to have but slight hydrating power in solution, and it should, therefore, have a high migration velocity; but this has been found to be slightly less than that of the halogens.

7. ACTION OF A SALT WITH HYDRATING POWER ON ANOTHER SALT IN THE SAME SOLUTION.

Jones and Stine [80] studied the action of a salt with hydrating power on the complexity of the hydrates formed by another salt present in the same solution. The pairs of salts investigated are potassium chloride and calcium chloride, calcium chloride and magnesium chloride, calcium chloride and strontium chloride, magnesium nitrate and strontium nitrate, magnesium nitrate and calcium nitrate, aluminium chloride and ferric chloride, calcium chloride and calcium nitrate, sodium bromide and lithium bromide, and a pair of salts which form only the simplest hydrates—potassium chloride and ammonium chloride. The problem consisted in calculating the approximate composition of the hydrates which are formed by the two substances when they are simultaneously present in the solution. It is obvious that the difficulties are much greater in this case than simply to calculate the approximate composition of the hydrates formed when this is only one substance present in the solution.

By taking into account, experimentally and theoretically, all of the many factors involved, considerable light was, however, thrown on this problem. The action of one salt with a common ion on the conductivity of a second salt was calculated from the law of mass action. We developed the formula for calculating the relation between freezing-point lowering and hydration if only one salt formed hydrates; and also the formula when both salts form hydrates.

The salts were obviously so chosen as to give us the opportunity to study a great variety of conditions. The first two have a common anion, and only one has any appreciable hydrating power. One of these salts is a binary, and the other a ternary electrolyte. The next four pairs are ternary electrolytes with a common anion; and both of the members of each of these pairs have large hydrating power. The next two salts are quarternary electrolytes with a common anion, and both have great hydrating power. The next two have a common cation. The last pair but one has a common anion, and both salts show considerable hydrating power; while the two members of the last pair have a common cation, and neither shows any considerable hydrating power.

[80] *Amer. Chem. Journ.*, 39, 313 (1908).

It was found that when two hydrated salts are mixed each dehydrates the other to some extent, the amount being controlled by the law of mass action. This would be the case only if the calculated composition of the hydrates was approximately correct.

It was further shown that the ions and molecules have very different hydrating power. While in most cases the ions have the greater hydrating power, in some special cases the molecules seem to have the greater power to combine with water.

Some interesting results were obtained when potassium chloride and ammonium chloride were mixed; both of these salts having only slight hydrating power. If two salts with a common ion are mixed, each drives back the conductivity of the other, and it has been assumed that this is due almost entirely to a suppression of the dissociation. If this were the complete explanation, we would have the greatest effect on the conductivity when the salts in question were most strongly dissociated. Since the dissociation at zero degrees is greater than at 25°, the diminution in the conductivity should be greater at the lower temperature.

The fact is exactly the opposite. There is a very small suppression of the ionization at zero, a more marked action at 12°; and at 25° there is a very pronounced difference between the conductivity of the mixture and the sum of the conductivities of the constituents. It is therefore obvious that the suppression of the ionization is not the only factor which comes into play here. This is made perfectly obvious by the fact that a number of the above-named solutions are practically isohydric.

Other factors which can come into play are:

The change in the viscosity of the solution produced by mixing the two salts. The change in the size and mass of the ionic spheres, due to the change in the hydration caused by mixing the two salts.

The action of one salt on the other present in the same solution is, thus, not as simple as was assumed, there being several factors coming into play. For details of this work see Publication of the Carnegie Institution of Washington, No. 180.

8. WORK IN MIXED SOLVENTS.

The work in mixed solvents, including water, methyl alcohol, ethyl alcohol, acetone, and glycerol, and mixtures of these solvents with one another, has been in progress in this laboratory contin-

uously for a dozen years. This work has been carried out by my co-operators, Lindsay,[31] Carroll,[32] Bingham,[33] Bassett,[34] Rouiller,[35] McMaster,[36] Veazey,[37] Kreider,[38] Mahin,[39] Schmidt,[40] Guy,[41] and Davis.[42] This work has been published collectively by the Carnegie Institution of Washington.[43] A fairly large number of salts were investigated in the pure and in the mixed solvents, and results were obtained which bear directly upon the solvate theory of solution.

The conductivity of a salt like potassium iodide in mixtures of methyl alcohol and water has, in a particular mixture of these two solvents, a decided minimum. The significance of this minimum was satisfactorily explained by Jones and Murray.[44] They studied the effect of one associated solvent on the association of another associated solvent in the following manner. They determined the molecular weight of acetic acid dissolved in formic acid, changing the dilution of the acetic acid. These are both associated solvents, and neither appreciably dissociates the other. They found that the molecular weight decreases rapidly as the dilution of the solution increases. This shows that formic acid diminishes the association of acetic acid.

They then performed the converse experiment, using acetic acid as the solvent and dissolving formic acid in it, changing the dilution of the formic acid present. They found that the molecular weight of the formic acid became less and less as the dilution of the solution became greater and greater, showing that the acetic acid was breaking down the association of the formic acid. Thus, each of these two solvents breaks down the association of the other.

Then, water and acetic acid were studied in a similar manner.

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[31] *Amer. Chem. Journ.*, 28, 329 (1902).
[32] *Ibid.*, 32, 521 (1904).
[33] *Ibid.*, 34, 481 (1905).
[34] *Ibid.*, 32, 409 (1904).
[35] *Ibid.*, 36, 440 (1906).
[36] *Ibid.*, 36, 325 (1906).
[37] *Zeit. phys. Chem.*, 61, 641 (1908); 62, 44 (1908).
[38] *Amer. Chem. Journ.*, 45, 282 (1911).
[39] *Ibid.*, 41, 433 (1909); *Zeit. phys. Chem.*, 69, 389 (1909).
[40] *Amer. Chem. Journ.*, 42, 37 (1909).
[41] *Ibid.*, 46, 131 (1911).
[42] *Zeit. phys. Chem.*, 81, 68 (1912).
[43] Carnegie Institution of Washington, Publications Nos. 80 and 180.
[44] *Amer. Chem. Journ.*, 30, 193 (1903).

Water dissociates acetic acid only slightly. It was found that each of these solvents breaks down the association of the other; similarly, water and formic acid each breaks down the association of the other. Jones and Murray conclude from this work that associated solvents in general diminish each other's association. Indeed, this is what common-sense would suggest as highly probable. An associated solvent, as is well known, breaks down the molecules of dissolved electrolytes into their ions. Similarly, an associated solvent breaks down the molecules of nonelectrolytes dissolved in it, not into ions, since that is not possible, but into the simplest molecules. Since each of the two associated solvents diminishes the association of the other, each diminishes the dissociating power of the other, in terms of the well-known relation between the association of a solvent and its dissociating power. Consequently, two associated solvents, such as water and methyl alcohol, when mixed, possess less dissociating power than would be calculated from the composition of the mixture and the law of averages. A substance dissolved in a mixture of two associated solvents will show a conductivity minimum in that particular mixture in which each solvent lowers the association of the other to the greatest extent; or at least, the sum of the two lowerings of the association is a maximum. This also explains why it is that a salt dissolved in a mixture of water and methyl alcohol may have in the proper mixtures a smaller molecular conductivity than in the pure methyl alcohol alone. Each solvent diminishes the association of the other, and, consequently, its dissociating power. When acetone was used as one of the solvents the minimum did not appear, but a pronounced *maximum* in the conductivity curve manifested itself. The maximum was very pronounced when lithium nitrate or calcium nitrate was used, and when a mixture of acetone with methyl or ethyl alcohol was employed as the solvent. It was shown theoretically that this maximum must have one of two causes: It must be due either to an increase in the dissociation increasing the number of ions present; or to a diminution in the size of the ionic spheres, accelerating the velocity of the ions. It is easy to eliminate one of these factors. The direct measurement of the dissociation in mixtures of the above-named solvents shows that such mixtures do not dissociate to a greater extent than would be calculated from the dissociating powers of the individual solvents. Having excluded this factor, we are forced to conclude that the conductivity maximum is caused

by a change in the solvation of the ion, or the amount of the solvent with which the ion is combined.

In dealing with the conductivity in pure solvents, as well as in the mixtures of these with one another, we must therefore take into account the magnitude of the spheres of the solvent surrounding the ions, and especially any changes in the magnitudes of these spheres in the different mixtures of the solvents. Every change in the magnitude of these spheres would produce a change in the effective masses of the ions, and, consequently, a change in the velocities with which they move.

The magnitude of the ionic spheres is an important factor in conditioning the conductivity, and changes in the magnitudes of these spheres in the different mixtures of the solvents are the most important factor in producing the maximum in the conductivity curves. The maximum occurs in that mixture where the ionic spheres are a minimum. This seems to be the only possible explanation of the maximum. The relation of the solvate theory to the temperature coefficients of conductivity in nonaqueous and in mixed solvents, is just as important as the relation between hydration and the temperature coefficients of conductivity in aqueous solutions. Since these relations have already been fully discussed for aqueous solutions, the discussion will not be repeated for nonaqueous solutions. For this reference must be had to the Carnegie Publications above referred to.[45]

Evidence was furnished by the work of Schmidt, Guy and Davis,[45] that glycerol also has the power to combine to some extent with certain substances dissolved in it. It would, however, lead us too far here to discuss this in any detail. Here, again, reference only can be made to the collective publications of these researches.

One other fact was discovered by Jones and McMaster, working in mixed solvents, to which brief reference will be made. It was found that certain salts in certain mixtures of certain solvents have *negative temperature coefficients of conductivity*. This is true of cobalt chloride in the 75 per cent. mixture of acetone with methyl alcohol; and also in the 50 and 75 per cent. mixtures of acetone with ethyl alcohol. Negative temperature coefficients of conductivity had been observed at low temperatures; but this seems to have been the first time that they were observed at ordinary temperatures. What do they mean?

[45] Publications Carnegie Institution of Washington, Nos. 80 and 180.

With rise in temperature the solvent becomes less viscous, increasing the velocity of the ions. With rise in temperature the association of the solvent becomes less, and, consequently, its dissociating power; which means that at the higher temperature there would be a smaller number of ions present in the solution. These two influences act counter to one another, the former increasing the conductivity and the latter diminishing it. When the temperature coefficient of conductivity is negative, it means that the decrease in the number of ions with rise in temperature more than counterbalances the effect on conductivity of the increased velocity with which the ions move. This explanation accounts very satisfactorily for the results in nonaqueous solvents. The alcohols and acetone are, at ordinary temperatures, highly associated liquids. Rise in temperature diminishes their association, and, consequently, their dissociating power.

Jones and McMaster found that a solution of cobalt chloride, $v = 200$, in a mixture of 75 per cent. acetone with methyl alcohol has a *zero temperature coefficient of conductivity*. It was found that in nonaqueous solvents, as well as in water, certain salts, especially those of potassium, rubidium, and cæsium, *lower the viscosity of the solvent in which they are dissolved*. Jones and Veazey explained this fact in the same way that they did the corresponding fact in water. If the ionic volume of the dissolved ion is much larger than the molecular volume of the solvent molecules, the effect would be to diminish the frictional surfaces that would come in contact, and consequently to diminish the friction when the molecules move over one another.

It is well known that potassium, rubidium, and cæsium occupy the maxima on the atomic volume curve. Here, again, for details reference must be had to the Publications of the Carnegie Institution of Washington, Nos. 80 and 180.

9. EVIDENCE FOR SOLVATION BASED UPON THE POWER OF SOLUTIONS TO ABSORB LIGHT.[46]

A brief account of some of our work on the *absorption spectra of solutions* has already been published in this journal.[47] This

[46] All of the work herein described on the absorption spectra of solutions, and a large amount which cannot even be here referred to, have been carried out with the aid of grants from the Carnegie Institution of Washington to H. C. Jones. (See Publications of the Carnegie Institution of Washington, Nos. 60, 110, 130, 160, and 190.)

[47] JOURNAL OF THE FRANKLIN INSTITUTE, 173, 228 (1912).

was, however, far too brief to give any adequate conception of the work done or the results obtained. It may not at first sight seem obvious how a study of the power of solutions to absorb light could bear on the solvate theory of solution. A moment's thought will show how this is the case.

The absorption of light by substances in solution is a resonance phenomenon. Something in the solution must be thrown into resonance by any given wave-length of light, in order that that wave-length may be stopped. If an ether vibration of given wave-length finds something in the solution which it can set vibrating, the energy in that particular wave-length is expended in setting up the new vibration, or the light of this wave-length is, as we say, absorbed. If all of the wave-lengths of light find something which they can throw into resonance with themselves, they are all stopped, or the solution is, as we say, *opaque*. If none of the wave-lengths of light find anything in the solution which they can throw into resonance, none of them are stopped, or the solution is, as we say, transparent. Resonance causes opacity; the lack of resonance, transparency. The color of solutions is, then, due to the fact that certain wave-lengths of light are absorbed by the solution, while others pass on through. Those that pass on through give the color to the solution in question. The thing in the solution which is thrown into resonance by the ether vibrations impinging upon it is called the resonator. It was supposed until recently that this was the ion, which is a charged atom or group of atoms. Since the atom has been shown by Thomson to be a complex system; and since he has shown in what its complexity consists, viz., electrical charges, we have about come to the conclusion that it is these electrical charges or electrons which are the resonators or absorbers of light. However this may be, the fact pointed out above is true; that the absorption of light by dissolved substances is due to a resonator in the solution being thrown into resonance with the wave-lengths of light that are absorbed. This resonator, whatever it is, would probably have different resonance when anhydrous than when combined with more or less of the solvent; and, further, the resonance would be different when different amounts of the solvent were combined with the resonator.

We can now see how a study of the absorption spectra of solutions could throw light on the nature of solution. The anhydrous

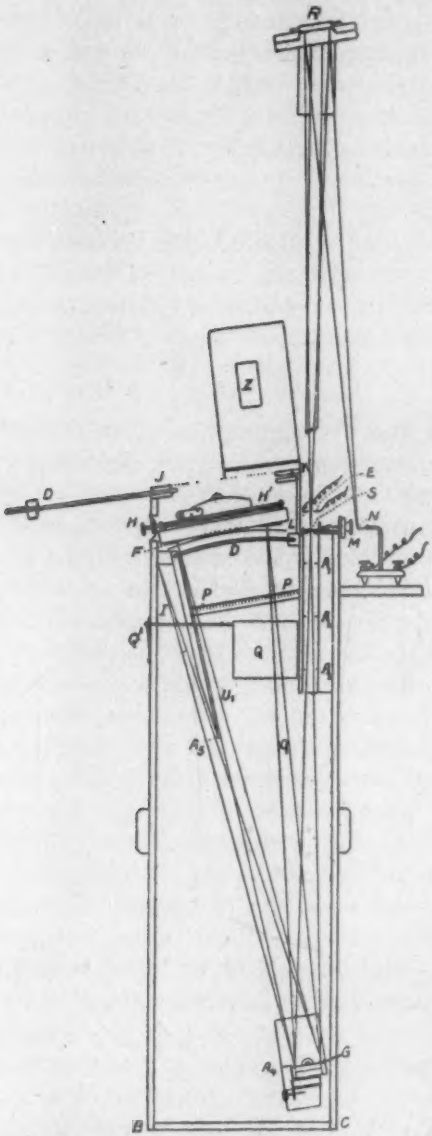
resonator should have different absorption from the hydrated resonator. If we vary the amount of water in combination with the resonator we should change the absorption spectra of the solution. There are, as we shall see, a number of ways of doing this, and marked changes in the absorption spectra have resulted. Further, when a salt is dissolved in a given solvent, it combines with some of that solvent. In water we have hydrates; in alcohol we have alcoholates; in glycerol, glycerolates, etc., we should expect the resonator to be affected differently by the different kinds of solvates around it. In a word, we should expect a salt dissolved in different solvents to have different absorption spectra. We shall learn that such is the case.

10. WORK OF JONES AND UHLER.

Work on the absorption spectra of solutions has been in progress in this laboratory continuously for eight years, under grants from the Carnegie Institution of Washington. The experimental work at first consisted in allowing white light from a Nernst glower to pass through a solution, then fall on a concave grating, and then upon a photographic plate. The wave-lengths that were absorbed by the solution would appear as dark lines or bands upon the photographic plate. About *eight thousand* solutions have already been studied. The apparatus used by Jones and Uhler,[48] who first worked on absorption spectra, is shown in Fig. 3, which is one-fifth the natural size. Light from the Nernst glower, N, is concentrated on the slit S by the concave mirror R. It then passes to the Rowland grating G. From this a part of the light is sent to the photographic film F. The slit-width is regulated by the micrometer screw M. Q_1 and Q_2 are screens. If Q_2 is perpendicular the light passes directly to the film. If Q_1 is horizontal, only ultraviolet light of wave-length shorter than 0.4 μ reaches the film. H and H_1 are a toothed-wheel system for moving non-exposed parts of the plate successively into the path of the light from the grating. Q and Q_1 are doors leading into the spectroscope. Several black diaphragms and screens, A_1, A_2, A_3, etc., protect the photographic film from all spectra with the exception of that which is desired. U_1 and O_1 are the extreme rays of the spectrum of the first order, which can be investigated.

[48] *Amer. Chem. Journ.*, 37, 138 (1907).

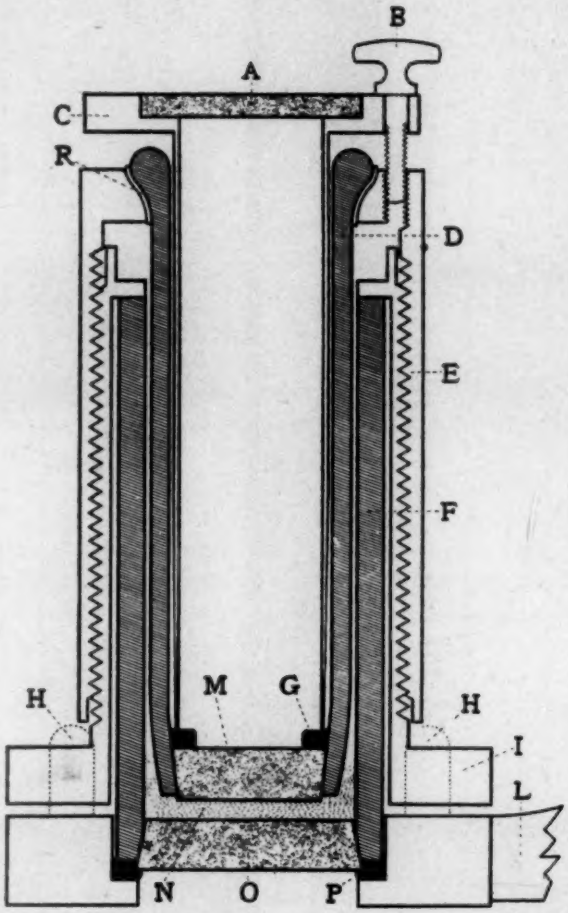
FIG. 3.



Jones and Uhler constructed a number of forms of cells for this work. They will not be described here in detail. Suffice it to say here that they were provided with quartz ends so as to

transmit the ultraviolet light. A cell was devised for non-aqueous solutions [48] which was free from all cement. The principle consisted in this; that conical pieces of quartz were carefully

FIG. 4.



ground into the ends of glass tubes and held in position by suitable mechanical arrangements.

A vertical section of the cell, enlarged to twice the natural

[48] *Amer. Chem. Journ.*, 34, 246 (1907).

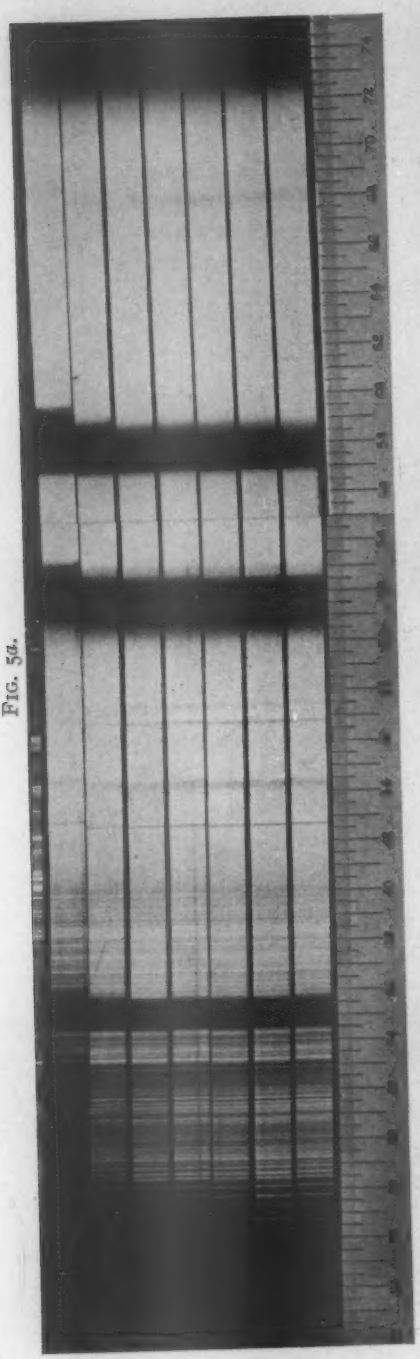


FIG. 5a.

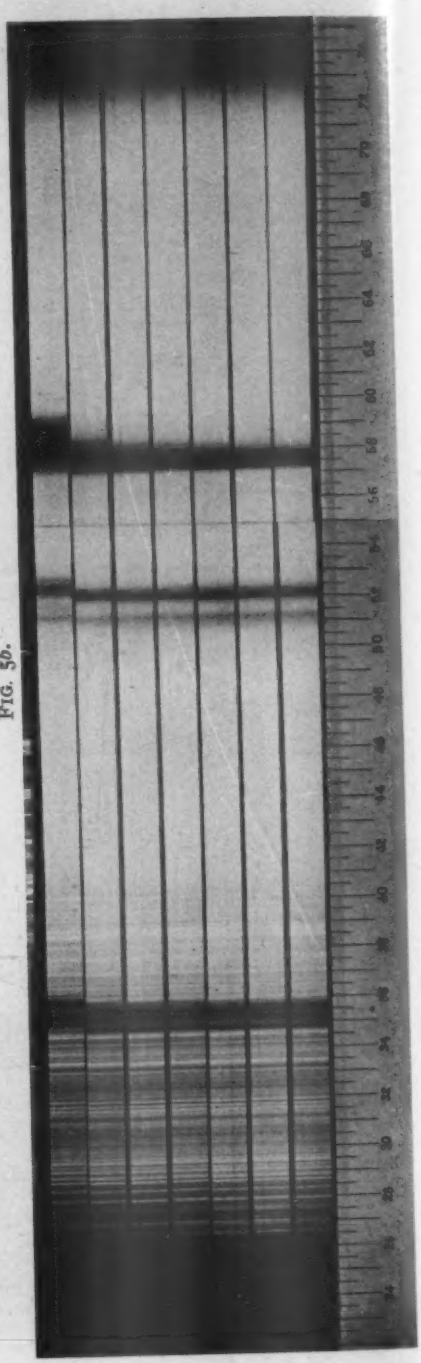


FIG. 5b.

size, is shown by Fig. 5, and the details of the several parts may be explained as follows: In its fundamental principles, the cell consisted of three distinct parts: (*a*) An outer glass tube with a quartz bottom to hold the liquid; (*b*) an inner glass tube with a quartz plate at the lower end to regulate the depth of the liquid, and to cause the upper surface of the absorbing layer of solution to be both plane and parallel to the quartz bottom of the larger glass tube; (*c*) a mechanism which would act as a stopper to the system of glass and quartz just mentioned, and which would also enable the experimenter to adjust the cell for any desired depth of absorbing layer from zero to the full capacity of the cell,—*i.e.*, about 3.5 cm.

The separate parts of this piece of apparatus will be described in the order in which they would be assembled for actual use. *M* denotes a plane parallel plate of quartz, ground carefully in the form of a frustum of a cone, so as to fit very accurately into the conical hole at the lower end of the glass tube *D*. The thickness of this quartz plate was 4.6 mm., and its least diameter was 12.6 mm. The glass tube was blown with a thick shoulder at its upper end. The plate *M* was first slipped into place in the tube *D*, and then the rubber washer *B* was pushed down against the quartz by introducing the brass tube *C* into the glass tube. In order to prevent dust from entering the inner tubes, the plane parallel quartz plate *A* was permanently set into a cylindrical depression in the upper end of the glass tube *C*. This plate was 2 mm. thick and 20 mm. in diameter.

The brass tube widened out into a sort of plate at its upper end, and this projection was pierced by three holes at the vertices of an equilateral triangle. Through these holes suitable screws passed, and one of these is shown at *B*, Fig. 4. After the brass tube *C* had been introduced into the glass tube, the washer *R*, made of blotting-paper, was slipped up over the outside of the glass tube, until it would not pass through the shoulder of this tube. Then the group of parts thus far described was let down through the hole at the upper end of the hollow brass cylinder *E*, as far as it could go,—*i.e.*, until the washer *R* was tightly squeezed between the glass and brass surfaces. The three screws were next pushed through their respective holes, and turned until the quartz plate *M* was forced, liquid-tight, into the conical hole in the glass tube; care being taken at the same time to so adjust the system as to

have the axis of rotation of the glass tube and quartz plate parallel to the axis of the brass cylinder *E*. A thread of convenient pitch had been accurately cut in the inner surface of this cylinder. The purpose of this thread, as well as that of a fine line or groove which had been turned on the outside of the cylinder, in a plane at right angles to the axis of the latter, will be explained below.

Whenever the cell had been entirely taken apart, which was not often necessary, the distance between the plane of the lower surface of the quartz plate *M*, and the plane of the lower end of the cylinder *E*, had to be measured and recorded, since this distance varied with the thickness of the two washers and with the pressure exerted by the screws. The number expressing this distance was one of several numbers that had to be known in order to adjust the cell for a given depth.

The thread at *E* was next fitted to the thread that had been accurately cut to fit it on the outside of the brass cylinder *I*. Then the two cylinders were screwed together until the distance between the fine cut around the outside of *E*, and a certain point of the upper plane surface of the flange at the bottom of the cylinder *I*, had the proper value. This distance was, of course, measured along a generating line of the outer surface at *E* and, therefore, perpendicular to the plane just located. The assemblage of parts explained above formed a complete system in itself, and comprised all of parts *L* and *C*, using the notation of the remarks introductory to the more detailed discussion of the cell. The flange at the bottom of *I* was provided with three large and two small holes, and all of them pierced it parallel to the axis of the cylinder. The larger holes fitted closely over three pillars, *H* and *H*, while the smaller ones corresponded to two little screws. The pillars and screws were not in the plane of the diagram. The object of the pillars and screws will be explained a little later. The cylinder *I* was also turned so as to have a collar on its interior near the top.

When the desired depth of absorbing liquid had been determined upon the basis of intensity of color, etc., the distance between the line around *E* and the upper plane of the flange of *I* was found by the addition of three numbers. One of these was a constant of the apparatus, 1.34 cm., and the other two expressed, respectively, the required depth of solution, and the distance from the lower plane surface of the quartz plates *M* to the plane of the

lower end of the brass cylinder *E*. As an example from practice, for a depth of 2 cm. the sum was 1.34 + 2.00 + 0.69 = 4.03 cm.,—*i.e.*, the two cylinders *E* and *I* had to be screwed around each other until the line to the flange was equal to 4.03 cm.

Conversely, knowing this distance as well as the two cell data, it was merely a matter of algebraic addition to obtain the effective depth of the cell.

The remaining parts of the apparatus had the characteristics described below, and were assembled as follows: *L* denotes the handle of a stout, hollow, cylindrical plate, which formed the bottom of the complete cell. The interior of this plate was turned out so as to leave a flange at the bottom upon which the rubber washer *P* was placed. The three pillars mentioned above projected vertically from, and were rigidly attached to the plate *L*. Two holes had been tapped out of this plate to correspond accurately to the smooth holes of the flange of *I*. After laying the washer *P*, on the flange of *L*, and after pushing and turning the quartz plate *M* tight up into the conical holes of the glass tube *F*, the transparent system was set vertically with its lower end resting symmetrically on the washer. The thickness and the smallest diameter of this quartz plate were, respectively, 4.6 mm. and 19 mm. The solution to be studied, *N*, was next poured into the vessel constituted by *F* and *O*. It was necessary to measure the depth of the liquid, and it was found convenient to make this depth 2 mm. greater than the effective depth of the cell.

The assembled system of parts *A*, *B*, *C*, *D*, *G*, *I*, *M*, *R* was next let down over the glass tube *F*, until the upper flange inside the cylinder *I* rested on top of this tube. The three pillars *H* guided the system into the correct position, and prevented any rotation of the cylinders *I* and *L* around each other. Lastly, the two little screws were passed through the holes in the lower rim of *I*, and the two cylinders were screwed tightly together. This operation completed the adjustment of the cell. It is seen at once, from the preceding explanation, that the liquid or solution in question came only in contact with glass and quartz surfaces; while the vapor of the solutions studied did not act on brass, glass and quartz, and since the apparatus did not leak, the cell gave entire satisfaction. For vapors which would attack brass, but not the silicates, it is easy to see how a system could be designed which would differ from the one just described in

having coaxial glass tubes dip into a trap of some neutral liquid, instead of the brass cylinders *E* and *I*. Moreover, it would be quite possible to design the parts of the cell in such a way as to impart to the liquid the shape of a wedge or prism of adjustable angle and depth.

The work of Jones and Uhler had to do with three classes of facts, as we shall see. They studied the effect on the absorption, of *increasing the concentration of the solution*. They found that with increasing concentration of the solution the *absorption bands widened*. With increasing concentration of solutions of cobalt chloride, the absorption in the ultraviolet widened. The absorption bands in the green also became broader. Similarly, the ultraviolet absorption of copper chloride became broader with increasing concentration; and also the bands in the red. The bands of copper bromide also became broader with increasing concentration.

In interpreting the spectrograms, we must take into account the difference between the observed broadening of the absorption bands, and the broadening which would theoretically result if a change in concentration produced only an increase in the number of absorbing parts per unit volume, and not an increase in their active mass. The well-known theoretical formula, expressing the law of Beer and Lambert, is $J = J\hat{o}adc$, where d is the thickness of the absorbing layer and c the concentration. To test this law, it is necessary to vary the depth of the layer of the solution, in the same way and to the same extent as the dilution is varied. Jones and Uhler also studied the effect on absorption spectra of adding a *dehydrating agent in the form of a second salt*. The result was a *widening of the bands*. The absorption bands of cobalt chloride in the ultraviolet and green became wider as the amount of calcium chloride added increased. In this work the amount of cobalt chloride was kept constant, while the mass of the dehydrating agent was varied. The same result was obtained with cobalt chloride and copper chloride, to which increasing amounts of aluminium chloride were added.

The third point tested by Jones and Uhler was the effect of the addition of water to solutions in nonaqueous solvents. Thus, to solutions of salts in methyl alcohol, ethyl alcohol and acetone, different amounts of water were added, and the corresponding spectrograms photographed. The action of water was to *narrow the absorption bands*.

These facts were all interpreted in terms of the solvate theory of solution. Since, however, so much more direct evidence for the theory has been furnished by subsequent experimental work, these results will not be discussed in any detail.

II. WORK OF JONES AND ANDERSON ON THE ABSORPTION SPECTRA OF SOLUTIONS.

The second investigation in this laboratory on the absorption spectra of solutions was carried out by Jones and Anderson.[49] They used essentially the same apparatus that had been employed by Jones and Uhler, enlarging the spectroscope so as to extend from $\lambda 2000$ to $\lambda 7600$. The Nernst glower was employed for wave-lengths longer than $\lambda 3200$, and a spark for the shorter wave-lengths. It was necessary to have a spark with a very large number of lines, but without any lines of very great intensity. Carbon terminals, saturated with ammonium molybdate and uranium nitrate, gave the desired result.

Jones and Anderson worked in terms of Beer's law with solutions of salts of cobalt, nickel, copper, iron, chromium, neodymium, praseodymium, and erbium. In all they studied about 1200 solutions.

The salts of cobalt show one region of absorption in the ultraviolet and one in the green. The bands in the ultraviolet narrow with dilution in all cases where the conditions of Beer's law are fulfilled. It, however, remains constant when the molecules are kept constant. This would indicate that the absorber or resonator here is attached to, or is a part of the undissociated molecule, or the undissociated molecule itself. The bands near $\lambda 3300$ quickly disappear as the dilution is increased, even if the molecules in the path of the beam of light are kept constant. Its intensity increases rapidly with rising temperature. These bands cannot, therefore, be produced by molecules, but are *probably due to relatively simple hydrates*. Rise in temperature causes the complex hydrates to decompose into relatively simple hydrates, thus increasing the intensity of the band. Increase in the dilution increases the complexity of the hydrates, and thus causes the band to disappear. These facts all point to the conclusion that the band is due to *relatively simple hydrates*.

[49] Carnegie Institution of Washington, Publication No. 110. *Amer. Chem. Journ.*, 41, 163, 276 (1909).

The green cobalt bands appear in all aqueous solutions of cobalt salts, yet with different intensities. If these bands were due to the cobalt ions, they would have the greatest intensities in those solutions which are most strongly dissociated,—*i.e.*, in the most dilute solutions; the product of concentration times depth of layer being kept constant. For twice normal solutions the cobalt salts arrange themselves in the following order with respect to the increasing intensity of the green bands; nitrate, bromide, chloride, sulphocyanate. For one-tenth to two-tenths normal solution the sequence is; bromide, chloride, nitrate, sulphate, acetate, sulphocyanate. The order of their increasing dissociation is; acetate, sulphate, sulphocyanate, nitrate, chloride, bromide—which is almost the reverse of the above. This band, therefore, cannot be due to the cobalt ion. We found, however, that if the concentration of the sulphate is varied from 0.55 to 0.60 normal, which would change very little the dissociation, and the light passed through depths of layer of the solution such that the product of depth times concentration is a constant, the breadth of the green cobalt band does not change. This shows that the absorption producing this band is simply proportional to the number of cobalt atoms in the solution, regardless of their hydration. The green cobalt bands are therefore due to the cobalt atoms; the intensity of the absorption depends, however, on what these atoms are combined with. Aqueous solutions of cobalt salts absorb very little in the red, if they are not concentrated, or if they are hot. The presence of red absorption in solutions of medium concentration shows that this is not due to the ions. That there is red absorption in very concentrated solutions, would lead us to suspect that it was due to molecular aggregates. But since the absorption in the red *increases with rising temperature*, and since molecular aggregates are broken down with rise in temperature, it follows that these aggregates are not the cause of the red absorption of cobalt salts. The conditions which cause the red absorption,—high concentration, high temperature, and presence of a dehydrating agent,—are the conditions which give rise to simple hydrates. That the absorption in the red depends on simple hydrates is made more probable by the following facts: All the anhydrous salts show absorption in the red, being blue; likewise, the salts with only a few molecules of water; while the salts with six molecules of water show no red absorption.

The chloride and bromide of cobalt were studied in methyl alcohol, ethyl alcohol, and acetone. The chloride, which in water has an absorption band at $\lambda 3300$, in the alcohols has two bands, $\lambda 3100$ and $\lambda 3600$. These bands quickly disappear with dilution, and resemble in their general properties the $\lambda 3300$ band in aqueous solutions. These bands have their origin in simple solvates. The green cobalt band is present in the nonaqueous solutions studied. This is what we would expect if it was due to the cobalt atom.

The absorption in the red is stronger in nonaqueous than in aqueous solutions, and the intensity increases in the following order: Methyl alcohol, ethyl alcohol, acetone. With increase in dilution the bands quickly narrow in methyl alcohol, more slowly in ethyl alcohol, and they remain almost constant in acetone. This cannot be explained on the ground of dissociation, but can easily be explained on the assumption of simple solvates; since the power to form solvates decreases in the order methyl alcohol, ethyl alcohol, acetone. In methyl alcohol we have the most complex solvate, and, consequently, the least intense absorption bands. We thus see that the absorption spectra of cobalt salts are complex, the different absorption bands being due to different causes. The ultraviolet bands are due to simple hydrates, the green bands to the cobalt atom, and the absorption in the red also to simple hydrates. The absorption bands of nickel salts behave like the green cobalt bands. The nickel chloride band $\lambda 3960$ shows a decided widening as we approach a saturated solution. It also widens on the addition of large amounts of calcium chloride or aluminium chloride. From our study of the green cobalt bands we concluded that it was due to the cobalt atom. We must conclude that the absorption bands of nickel are due chiefly to the nickel atom.

The absorption spectrum of copper salts is much simpler than that of cobalt, consisting of only three absorption bands. We will consider only the bands in the ultraviolet and in the red. The absorption in the ultraviolet decreases rapidly with the dilution, the product of concentration and depth of layer of the solution being kept constant. Therefore, this band cannot be due to ions, but must be due to molecules. It should be observed that the absorption decreases with the dilution even when the entire number of molecules in the path of the beam of light is kept constant. This shows that the absorbing power of a molecule is markedly

affected by its immediate surroundings. It might be assumed that this was due to the formation of molecular aggregates. That this is not the case, is shown by the fact that a rise in temperature has the same effect on this band as increasing the concentration of the solution. It is well known that molecular aggregates are broken down by rise in temperature, and this would cause a *decrease instead of an increase in the absorption.* On the other hand, increase in concentration would increase the magnitude of these aggregates; but this produces the same change in the absorption bands as rise in temperature. The magnitude of the solvation, on the contrary, is diminished both by increase in concentration and rise in temperature. We must therefore conclude that the ultraviolet absorption of copper salts depends upon the solvated molecules, and that the absorbing power of these molecules is less the more complex the solvates.

It should be stated that the absorption in the ultraviolet in aqueous solutions is smallest, and increases if we pass from methyl alcohol to ethyl alcohol. The change in the absorption with dilution is greatest in aqueous solutions, and decreases if we pass from methyl alcohol to ethyl alcohol. This is what we should expect, since the solvating power is greatest in water, and decreases from methyl alcohol to ethyl alcohol. Therefore, the solvates would become less complex as we proceed from water to methyl alcohol, to ethyl alcohol. Consequently, with change in dilution, there should be greater change in the composition of the solvates in the aqueous solutions than in solutions in methyl or ethyl alcohol, and such is the fact.

The red absorption bands of copper become somewhat narrower when the product of concentration and thickness of absorbing layer is kept constant, but broaden somewhat when the molecules are kept constant. Their intensity changes much less with the solvent than the intensity of the violet bands. We conclude that these bands, like the green cobalt bands, are due to the metal atom, whose absorbing power is affected only slightly by its immediate surroundings.

The behavior of the red copper bands in methyl alcohol, on adding water, is remarkable. The bands at first broaden, and then, when more water is added, decrease in breadth. When a small amount of water is added, simple hydrates are formed. On the addition of more water these would become more com-

plex. The absorption of light by the relatively simple hydrates formed when a small amount of water is added, is greater than the methyl alcoholates existing in the solution in methyl alcohol; therefore, the first action of the water is to broaden the bands. The subsequent narrowing of the bands on the further addition of water is due to the more complex hydrates formed under these conditions. Similarly, ethyl alcohol narrows the bands, as would be expected; since here the solvates are simpler than in methyl alcohol.

The most important and interesting results obtained by Jones and Anderson have to do with salts of neodymium and praseodymium. It was found that the chloride and bromide of neodymium, in aqueous solutions of all concentrations, give practically identical spectra. The spectrum of the nitrate differs considerably from that of the chloride and bromide, especially in concentrated solution. For every band in the solution of the chloride there is a corresponding band in the solution of the nitrate; but in the more concentrated solutions the bands have a very different appearance. The nitrate bands are much broader and more washed out than those of the chloride, but with increasing dilution they become similar to the chloride bands. That the dilute solutions of the different salts of neodymium would have similar absorption bands would be expected from the theory of electrolytic dissociation; but this theory can in no wise explain the behavior of the nitrate bands.

Our work on the absorption spectra of neodymium chloride in mixtures of alcohol and water, makes it very probable that the molecules as well as the ions of this salt undergo solvation in solution. This enables us to explain the results with the chloride, bromide, and nitrate, if we assume that the absorption bands, in the ultimate analysis, are due to electrons which exist in the neodymium atom, or are intimately connected with it. If the atoms are free, the electrons will respond to certain wave-lengths of light. If the atoms are combined with three chlorine atoms as in neodymium chloride, these chlorine atoms would affect the periods of the neodymium electrons, and, consequently, the absorbing power of the neodymium atom. If we dissolve a neodymium salt in a solvent which would have no direct action on the salt, but would allow its molecules free movement, we would not expect that the solvent would have any appreciable influence on the light-

absorbing power of the neodymium atom. On the other hand, a solvent like water, which forms complex hydrates with the salt, could exercise a very marked influence on the absorption spectra of the salt; and this effect would be greater the more complex the anion of the salt. Take a salt like neodymium chloride ($NdCl_3$), where there are only three foreign atoms to affect the periods of the neodymium electrons. If this salt were combined with ten molecules of water of hydration, then there would be 30 atoms of the solvent affecting the neodymium electrons within the neodymium atom. If we were dealing with the nitrate $Nd(NO)_3$, we would have 12 foreign atoms in addition to the 30 of water of hydration; and 12 to 30 is much greater than 3 to 30. This would lead us to suspect that the spectrum of the nitrate in concentrated solution would be very different from that of the chloride or bromide.

If we increase the dilution of the solution, all of the above salts will dissociate into neodymium cations which cause the absorption and the corresponding anions. The cation is combined with ten molecules of water, no matter from which neodymium salt it comes. The anions, now being separated from the cation, have little or no effect on the periods of the electrons in the neodymium system. The change produced by dissociation of the molecule in the entire number of atoms which affect the periods of the neodymium electrons, is greatest for the salt with the most complex anion. Therefore, those salts whose molecules consist of the largest number of atoms combined with the neodymium atom, as the nitrate, sulphate, and acetate, on dissociating, should show the greatest change in their absorption spectra. Such is the fact. The spectrum of the nitrate changes with the dilution far more than that of the chloride or bromide. This theory also explains why the spectra of all three salts in very dilute solutions, where they are practically completely dissociated, are practically the same.

The most important point brought out by the work of Jones and Anderson is the following: A salt like *neodymium chloride has a very different absorption spectrum in water from what it has in methyl alcohol.* (See Fig. 5.) If such a salt is dissolved in a mixture of alcohol and water, and the relative amounts of water varied from 100 per cent. to 15 or 20 per cent., no change is observed. If the water relative to the alcohol is still further

diminished, the resulting spectrum is a superposition of the spectra of the aqueous solution and of the alcoholic solution. The spectrum of the aqueous solution decreases in intensity as the amount of water present decreases, and at the same time the alcoholic spectrum increases in intensity. The exact composition of the mixed solvent, in which both of the spectra have the same intensity, depends somewhat on the concentration of the salt. In general, it is from 7 to 8 per cent. water.

The results that were obtained for neodymium chloride in methyl alcohol and in mixtures of methyl alcohol and water are shown in Fig. 5. The uppermost strip of *a* corresponds to a solution of neodymium chloride in pure methyl alcohol. The second strip corresponds to a solution of neodymium chloride of the same concentration in methyl alcohol containing 16⅔ per cent. of water. It will be seen that the absorption is very different in the pure alcohol from what it is in the mixed solvents. Succeeding strips correspond to the addition of more and more water. Strip 3 from the top corresponds to 33⅓ per cent. water, strip 4 to 50 per cent. water, strip 5 to 66⅔ per cent. water, strip 6 to 83⅓ per cent. water, and strip 7 to pure water.

It will be seen that the entire change in the absorption spectrum takes place on the addition of 16⅔ per cent. of water to the methyl alcohol, and that the absorption in water is quite different from in alcohol.

In order to determine whether there was simply a shift in the position of the alcohol bands on the addition of water, or whether there were really new absorption bands in the water, *b*, Fig. 5, was taken. In this case a much more dilute solution of neodymium chloride was used. In the uppermost strip we have again the salt dissolved in the pure alcohol. In the second strip we have the salt in a mixture of methyl alcohol and 16⅔ per cent. of water, and in the succeeding strips more and more water is present. A comparison of the uppermost strip with strip 2 will show that in the two cases we are dealing with very different absorption bands. The number and structure of the bands in the pure alcohol are very different from the bands when there is water present. In a word, the "water bands" are not the "alcohol bands" simply shifted in position, but *entirely different absorption bands.*

We have here, then, a well-defined "alcohol" spectrum and

a well-defined "water" spectrum of neodymium chloride, just as we predicted from the solvate theory should exist.

The addition of more than 16⅔ per cent. of water to the alcohol does not further change the absorption spectrum in the case of the more dilute, as in the case of the more concentrated solution of neodymium chloride.

So far as is known to me, this is the first case ever found of the effect of a nonabsorbing solvent on the absorption spectrum of a compound dissolved in it—of the existence of well-defined "solvent bands."

Having found that all of the change in the absorption spectrum was produced on adding 16⅔ per cent. of water, we determined to study this change in detail by adding very small and increasing amounts of water to the alcohol.

Fig. 6 represents the results obtained when neodymium chloride was dissolved in a mixture of methyl alcohol and water. The concentration of the neodymium chloride was constant = 0.5 normal. The percentages of water, beginning with the solution whose spectrum is adjacent to the numbered scale, were 0, 5.5, 10.6, 16, 21.3, 26.6, and 32. The depth of the solution throughout was 0.5 cm.

In the second strip the bands characteristic of the alcohol solution are much more prominent than those belonging to the aqueous solution, while in the third strip the reverse is true. This shows that the composition of the mixed solvent which gives the bands with about half their normal intensity is 7 to 8 per cent. water. There we have both the "alcohol" and the "water" bands coexisting, and they are seen to have very different structures—are very different bands. The "water" bands decrease in intensity as the amount of water present decreases.

Take next, solutions in mixtures of methyl alcohol and water. The results are shown in Fig. 7, the concentration of the neodymium chloride being 0.15 normal.

The strip next to the numbered scale corresponds to the pure alcohol. As we go away from the scale the strips correspond to more and more water. In strip 3, counting from the bottom, which corresponds to 5.3 per cent. of water, we have both the "water" and the "alcohol" bands of equal intensity. As we go up the spectrogram, corresponding to the presence of more and more water, the "water" bands become stronger and stronger and the alcohol bands weaker, and quickly disappear.

FIG. 6.

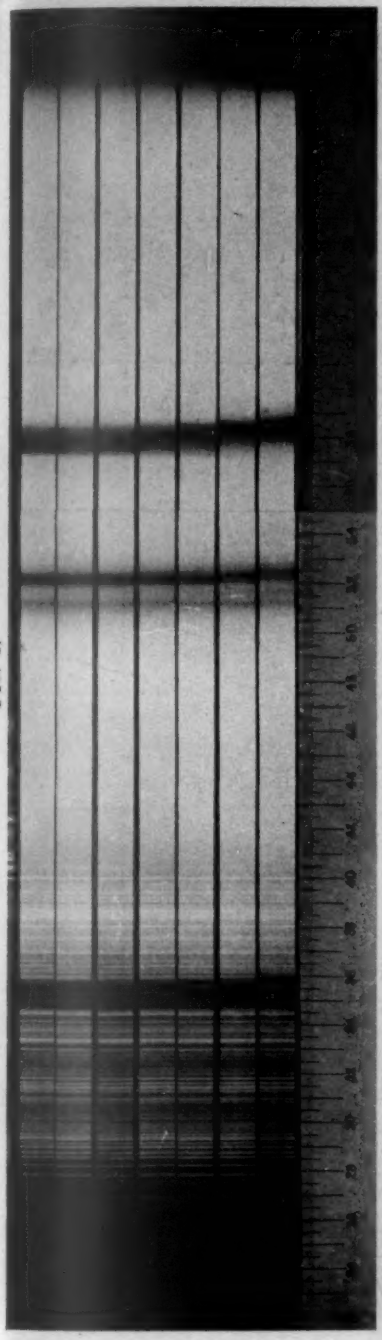


FIG. 6.

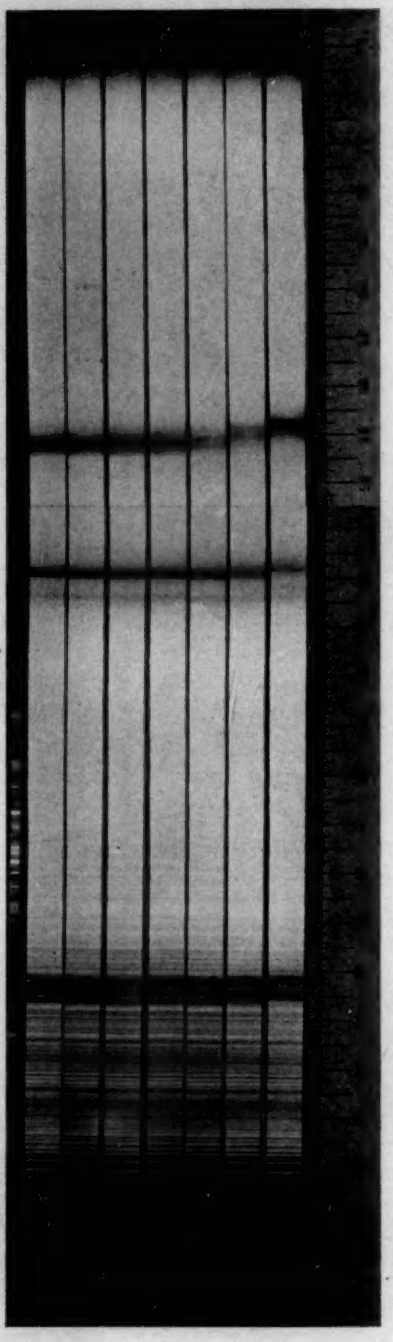


FIG. 7.

We have, then, in mixtures of water and methyl alcohol, as in mixtures of water and ethyl alcohol, perfectly definite absorption bands of neodymium chloride corresponding to each of the solvents present.

Jones and Anderson conclude, from their work, that the *facts which they have brought to light can be explained only in terms of the solvate theory of solution.* The different spectra in the different solvents are due to a combination between the solvents and the dissolved substances.

12. WORK OF JONES AND STRONG ON THE ABSORPTION SPECTRA OF SOLUTIONS.

Jones and Strong[50] continued the work on the absorption spectra of solutions for three years, and studied in all more than 4000 solutions. They studied neodymium and uranium salts in a great variety of solvents, and found a large number of examples of "solvent bands"—*i.e.*, where a salt dissolved in different solvents had different absorption spectra.

One of the best examples of "solvent" bands is Fig. 8. *a* is the spectrogram of uranous bromide in a mixture of water and methyl alcohol, and *b* is the spectrogram of uranous chloride in a mixture of water and methyl alcohol.

The aqueous solutions are at the bottom of the spectrograms, and as we go up more and more alcohol is added from strip to strip. We see the "water" bands strong at first, rapidly disappear; and the "alcohol" bands at first weak, increase in intensity as the amount of alcohol present relative to the water increases.

We have here *two entirely distinct sets of bands*, one corresponding to each of the solvents present. A better example than this of solvent bands could hardly be imagined.

Having found such abundant evidence of the effect of the solvent on the power of the dissolved substance to absorb light, in the case of the few solvents referred to above, it seemed very desirable to bring other solvents within the scope of this work, and this has been done. Since the neodymium absorption lines and bands are very sharp, it was selected as the principal substance to be used in this connection. This phase of the work has been carried out recently by Dr. Strong and myself.

[50] Carnegie Institution of Washington, Publications Nos. 130 and 160. *Amer. Chem. Journ.*, 43, 37, 97 (1910); 45, 1, 113 (1911); 47, 27, 85 (1912).

FIG. 8a.

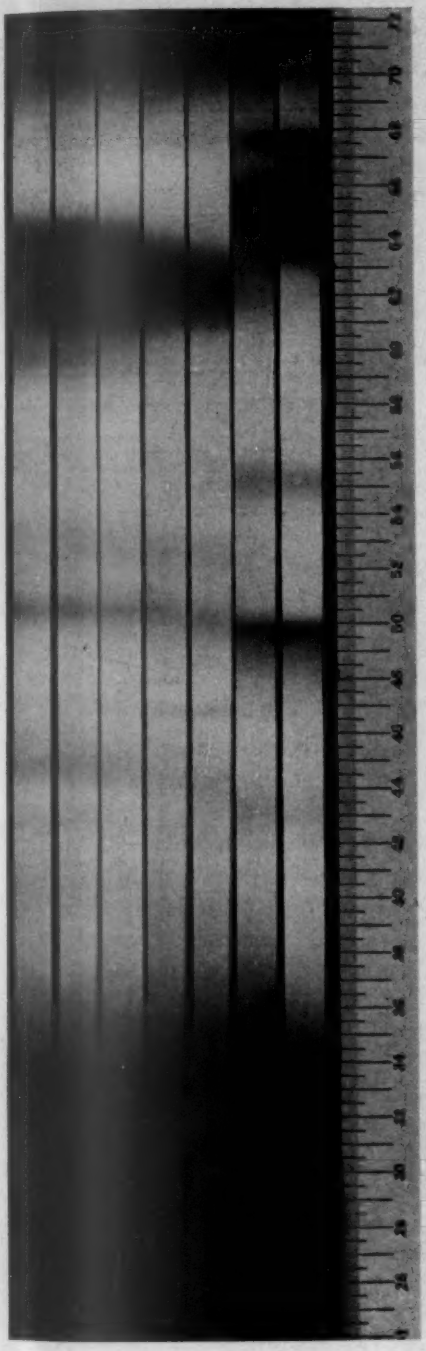


FIG. 8a.

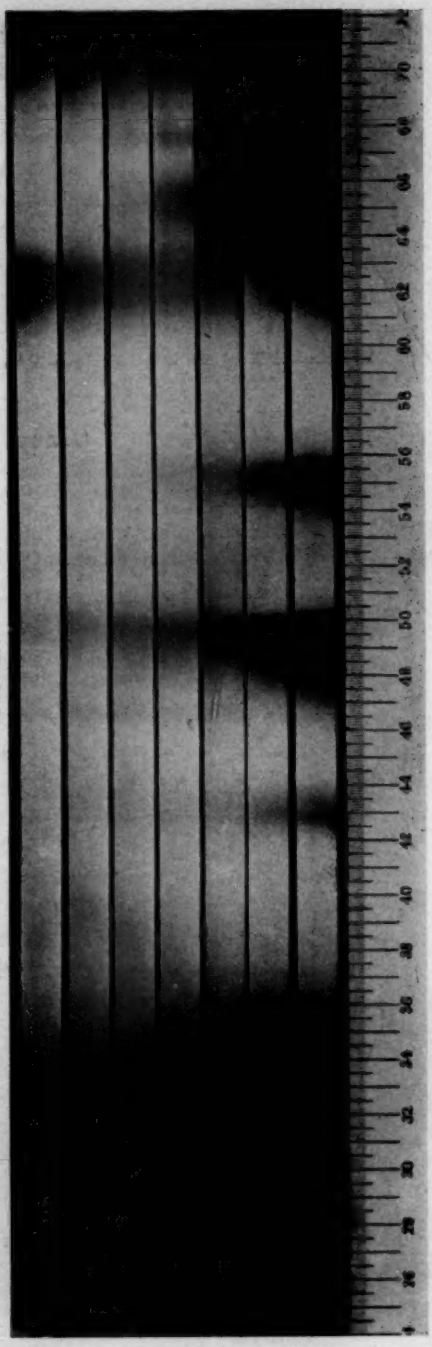


FIG. 8b.

Uranium Salts.[51]

An elaborate study was made of the absorption spectra of uranium salts, to see whether any evidence was obtainable for the existence of definite solvate bands in different solvents. We studied both uranyl and uranous compounds.

It was soon found that an aqueous solution of uranyl chloride shows absorption bands in different positions from those of solutions in methyl alcohol. These differences were sufficiently great to merit careful study.

What these differences are can be best seen by giving the wave-lengths of a few bands in the different solvents.

Uranyl Chloride.

In water	λλ 4025,	4170,	4315,	4460,	4560,	4740, and 4920
In methyl alcohol	λλ 4090,	4220,	4345,	4465,	4590,	4760, and 4930
In ethyl alcohol	λλ 4100,	4250,		4400,	4580,	4750, and 4900
In propyl alcohol	λλ 4100,	4230,		4400,	4580,	4750, and 4910
In isopropyl alcohol	λλ 4100,	4250,		4360,	4560,	4750
In butyl alcohol	λλ 4100,	4240,		4390,	4560,	4750, and 4970
In isobutyl alcohol				λλ4400,	4560,	4720, and 4900
In ether	λλ 4040,	4160,		4300,	4444,	and 4630
In methyl ester	λλ 4030,	4160,	4280,	4440,	4620,	4790, and 4920
In glycerol	λλ 4025,	4140,	4260,	4400,	4540,	4720, and 5050
In formamide				λλ4450,	4650,	and 4840

The absorption spectra of uranyl nitrate in mixtures of water and methyl alcohol were photographed. The absorption in pure methyl alcohol was much greater than in pure water. As water was added to the alcoholic solution the absorption became less and less. In the mixed solvents the bands became very broad. A careful study of the structure of these broad bands showed that they were the "water" and "alcohol" bands coexisting; and not one set of bands shifted in position, and this, as we shall see, is an important point.

A simple method of reducing uranyl to uranous salts in solution was found to be the action of nascent hydrogen. This was obtained by introducing into the aqueous solution of the uranyl salt a bar of zinc, and then adding the acid of the salt in question. In this way uranous salts could be prepared, and several of them were found to have sufficient stability for our purpose. Uranous

[51] The following pages are taken from a paper which recently appeared in the *Philosophical Magazine*.

chloride, uranous bromide, and uranous acetate were thus made and their absorption spectra photographed and studied. These salts proved to be very useful for the detection of "solvent" bands, or the effect of the solvent on the absorption spectra of salts dissolved in it. The uranous bands are numerous, and, what is far more important for our work, they are well defined, with comparatively sharp edges, and their wave-lengths can be accurately determined. In this respect they are second only to certain lines of neodymium. Some of the most conclusive evidence for solvation in solution, furnished by our spectroscopic work, was with the uranous salts.

The spectrum of uranous chloride in water is quite different from the spectrum in methyl alcohol, and this, in turn, very different from the spectrum in acetone. A glance at the plate for these solutions would lead us to conclude that we were dealing with three very different absorption spectra.

In a mixture of water and methyl alcohol, as the amount of water increases the water band $\lambda 6750$ comes out, gradually increasing in intensity. The methyl alcohol band $\lambda 5050$ to $\lambda 4850$, which is probably double, narrows on the red side into a band at $\lambda 4850$. Methyl alcohol bands $\lambda 4770$ and $\lambda 4600$ practically disappear and $\lambda 4670$ becomes very weak. In their places appear the water bands $\lambda 4700$ and $\lambda 4550$. The methyl alcohol band, $\lambda 4300$ to $\lambda 4450$, becomes weaker and breaks up into a band at $\lambda 4400$ and a band at $\lambda 4280$. The methyl alcohol bands $\lambda 4230$ and $\lambda 4120$ apparently come together, as the amount of water present relative to methyl alcohol increases, and becomes the water band at $\lambda 4160$.

It is thus obvious that the aqueous solution shows very different absorption bands from the solution of uranous chloride in methyl alcohol.

The addition of ethyl alcohol to an aqueous solution of uranous chloride produces a marked change in the spectrum, the ethyl alcohol bands being very different from the water bands. As the amount of ethyl alcohol present relative to water increases, the ethyl alcohol bands come out and the water bands gradually disappear.

The addition of acetone to a methyl alcohol solution of uranous

chloride brings out a number of "acetone" bands between λ6000 and λ6500. A strong absorption band also appears from λ6500 to λ6800. There is also an acetone band at λ5600.

The addition of acetone to a methyl alcohol solution of uranous chloride produces a marked change in the spectrum, the "acetone" bands being very different from the "water" bands. The acetone solution absorbs much less in the region λ6500. The aqueous solution has a characteristic band at λ6750. There are acetone bands at λ4920, λ4750, and λ4590; and water bands at λ4980, λ4700, and λ4570. The absorption of uranous chloride in ethyl alcohol is very similar to the absorption in methyl alcohol, as would be expected; the methyl alcohol bands being of slightly shorter wave-lengths.

The absorption spectrum of uranous chloride in glycerol was photographed, also when water was added to the glycerol solution.

The absorption spectrum in glycerol was found to be very different from what it was in water.

The absorption spectrum of uranous chloride in a mixture of methyl alcohol and ether was photographed. The methyl alcohol solution showed complete ultraviolet absorption to wave-length λ3700. The addition of ether increased the absorption, the absorption of the short wave-lengths extending now to λ3800.

In methyl alcohol there was considerable general absorption in the region λ4300. With the addition of ether the absorption was almost complete from λ4100 to λ4450. The addition of ether caused the uranyl bands to shift slightly towards the red without, however, changing their general character. The magnitude of this shift can be seen from the following table.

URANYL CHLORIDE BANDS IN METHYL ALCOHOL.

λλ 3880,	4000,	4110, 4135,	4240, 4285.	4400,	4610,	4780,	4930,	5050,

URANYL CHLORIDE IN METHYL ALCOHOL TO WHICH ETHER IS ADDED.

λλ 3890,	4010,	4140,	4260,	4440,	4630,	4790,	4960,	5050.

The effect of the presence of ether is thus very pronounced, not only causing the bands to shift slightly towards the red, but also increasing the amount of absorption.

It should be stated that in the work with the uranous salts there were present in the solution, in addition to the salt, a little of the free acid of the salt and a small amount of the zinc salt. While these probably had a slight effect on the absorption spectra, the effect must have been far too small to have produced such changes as those recorded above for the different solvents.

Having found such abundant evidence for the effect of the solvent on the power of the dissolved substance to absorb light, in the case of the few solvents referred to above, it seemed very desirable to bring other solvents within the scope of this work, and this has been done. Since the neodymium lines and bands are very sharp, it was selected as the principal substance to be used in studying the effect of the solvent on the absorption spectra of the dissolved substance, where a large number of solvents was to be employed. This phase of the work has been very recently carried out by Jones and Strong.

Absorption Spectra of Neodymium Salts.

The following nomenclature will be used in describing the neodymium absorption spectra:

α group in the region $\gamma 3400$ to $\gamma 3600$.
β " at about $\gamma 4300$.
γ " from $\gamma 4600$ to $\gamma 4800$.
δ " from $\gamma 5000$ to $\gamma 5400$.
ϵ " in the region $\gamma 5800$.
τ " at $\gamma 6300$.

In designating the neodymium spectra we start from the violet end of the spectrum. This is the natural method when a grating is used. It is doubtful whether, in the near future, the ultraviolet spectrum of neodymium can be studied much farther than we have done, so that this is the natural end of the spectrum at which to begin. It is, on the other hand, probable that there are many neodymium bands farther down in the infra-red than we have gone; and when these have been worked out they can then be named in the natural order.

The change in the absorption spectrum of neodymium chloride as the solvent is changed can be seen best by expressing the results in the following form. The abbreviations used are " d." diffuse,

" fa." faint, " fi." fine, " h." hazy, " i." intense, " n." narrow, " sh." sharp, " st." strong, " we." weak, " wi." wide.

The following results obtained with neodymium chloride show the effect of the solvent on the absorption spectra of solutions of this compound. The bands of the different solvents have different wave-lengths and different relative intensities.

Having found that the solvent played an important part in determining the absorption of light by the dissolved substances, Jones and Strong used *isomeric organic solvents* to see whether such closely related compounds would affect differently the power of substances dissolved in them to absorb light. They prepared solutions of neodymium chloride in propyl and isopropyl alcohols, and in butyl and isobutyl alcohols, and photographed the absorption spectra of this salt in these isomeric solvents. The following results show different absorption lines and bands in the isomeric solvents:

α GROUP.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 3390 we. 3465 n. st. 3505 n. st. 3540 n. st. 3560	λλ 3475 fa. 3505 3560 wi. i.	λλ 3545 sh. 3460 3490 3510 we. 3525 st. 3540 st. n. 3560 d. 3580 we.	λλ 3460 3510 3535	λλ 3450 sh. n. 3460 we. 3492 d. 3535 sh. n. 3545 3560 d.	λλ 3455 we. 3485 st. 3515 we. 3545 3570	λλ 3520 we. 3475 st. 3550 st.

β GROUP.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 4271 sh. 4290 n. we.	λλ 4290 4325	λλ 4270 we. 4285 4330 wi. we 4450 wi. we	λλ 4265	λλ 4265 4285 4300	λλ 4300 we.	λλ 4288 sh. 4270 fi. 4305 fi.

γ GROUP.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 4610 h. 4645 we. 4685 4755 sh. 4820 ni.	λλ 4700 4780 4825	λλ 4600 we. d. 4700 4770 4830	λλ 4600 d. 4690 4730	....	λλ 4700 4730 4780 4830 4880 we.	λλ 4620 4710 4730 4760 4790 4840

δ GROUP.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 5090 n.	λλ 5125 h.	λλ 5130 wi. d.	λλ 5100 wi. d.	λλ 5085 n.	λλ 5150	λλ 5120 wi. h.
5125 wi. h.	5180 h. fa.	5180 wi. d.	5320 wi. d.	5095 n. we.	5260	5170 n.
5205 i. n.	5220 i. n.	5220		5130	5215	5190 n.
5222 i. n.	5245 i.	5230		5200	5230	5230
5255 n.	5290 n.	5250		5215	5250	5240
5315 fa. h.	5315 fa.	5290		5240	5300	5250
		5330 we.		5270		5270 we.
				5300		

ε GROUP.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 5725 n. st.	λλ 5725 h.	λλ 5740	λλ 5720 d.	λλ 5750	λλ 5740 we.	λλ 5740 h.
5745 st.	5765 n.	5780	5780	5780	5810 st.	5790
5765 st.	5800 st.	5810	5810	5820	5850 st.	5805
5795	5835 i.	5850		5860	5890	5820
	5860 h.			5900	5920	5850
	5895 fa.			5930	5950 we.	
	5925 fa.				5995 we.	
					6020 we.	

If we compare carefully the spectra of neodymium chloride in butyl and isobutyl alcohols, we find that the bands are weak and diffuse in isobutyl alcohol, and have different relative intensities from what they have in the butyl alcohol. The bands in butyl alcohol are very much finer and sharper than they are in isobutyl alcohol. Further, the bands of neodymium chloride in isobutyl alcohol have slightly greater wave-lengths than in butyl alcohol.

To eliminate the possibility of the effect of the solvent on absorption spectra being due to anything inherent in the nature of neodymium chloride, the nitrate of neodymium was studied in the same way as the chloride.

The absorption spectra of neodymium nitrate in water, in methyl alcohol, in ethyl alcohol, in mixtures of these alcohols and water, in propyl and isopropyl alcohols, in butyl and isobutyl alcohols, in acetone and in mixtures of acetone and water, in ethyl ester and in formamide, were carefully photographed and studied. Results will be given in the case of neodymium nitrate only for the α bands.

α Bands.

In water. Practically the same as the bands of neodymium chloride, but the bands of the nitrate are broader and hazier than those of the chloride.

In methyl and ethyl alcohols. There are only two bands in the α group, λ3465 and λ3545.

In propyl alcohol. λλ3455, 3500, and 3585.

In isopropyl alcohol. λλ3460, 3505, and 3535.

In butyl alcohol. λλ3450, 3500, and 3540.

In isobutyl alcohol. Ultraviolet absorption was so great that on the plate taken the α group did not appear. The absorption in general is the same as that of the chloride in this alcohol.

In acetone. λλ3475 and 3555.

In ethyl ester. λλ3455, 3500, and 3540.

The other groups of absorption bands of neodymium nitrate in the different solvents show differences in the wave-lengths comparable with the above; but these results suffice to show the effect of the solvent on the power of neodymium nitrate to absorb light.

The above evidence that the solvent plays an important part in the absorption of light by substances dissolved in it is strong. When we take into account the number of salts studied and the number of solvents employed, the evidence is little short of proof. The only reasonable question is, How are we to interpret these facts? Before attempting to answer this question we should take into account also the following fact. A salt dissolved in a given solvent is characterized by a definite absorption spectrum. When a salt is dissolved in mixtures of varying proportions of two solvents *only two definite absorption spectra appear*, one being characteristic of each solvent. One spectrum *does not gradually change* into the other as the composition of the mixed solvent changes, but only the *relative intensities* of the two spectra vary. Starting with that mixture of the two solvents in which both of the spectra are equally intense, if we diminish the amount of *a* relative to *b*, the spectrum corresponding to *a* becomes feebler and feebler, and the spectrum corresponding to *b* more and more intense. This fact was first noted by Jones and Anderson, and since repeatedly confirmed by the work of Jones and Strong. We found that when neodymium chloride was dissolved in a mixture of methyl alcohol and water, it showed a definite set of "water" bands and a definite set of "methyl alcohol" bands. As the amount of water in the solution was

decreased relative to the alcohol, the "water" bands decreased in intensity but remained in the same position. As the amount of alcohol in the solution was decreased relative to the water the "alcohol" bands decreased in intensity, but their position remained unchanged.

Jones and Anderson interpreted these facts as strong evidence in favor of the view that there are definite hydrates and definite alcoholates in the solution.

The spectroscopic evidence for solvation in solution furnished by Jones and Anderson has, as has already been stated, been increased many fold by the work of Jones and Strong. A large number of solvents and a fairly large number of salts have been used, and the existence of solvent bands in general established.

The question of the relative stability of the different solvates with respect to various physical and chemical agents, has been studied at length by Jones and Strong by means of absorption lines and bands. It would lead us beyond the scope of this paper to discuss these results in detail. Suffice it to say that the hydrates in general are the most persistent of all the solvates, although this depends upon the conditions to which the solution is subjected.

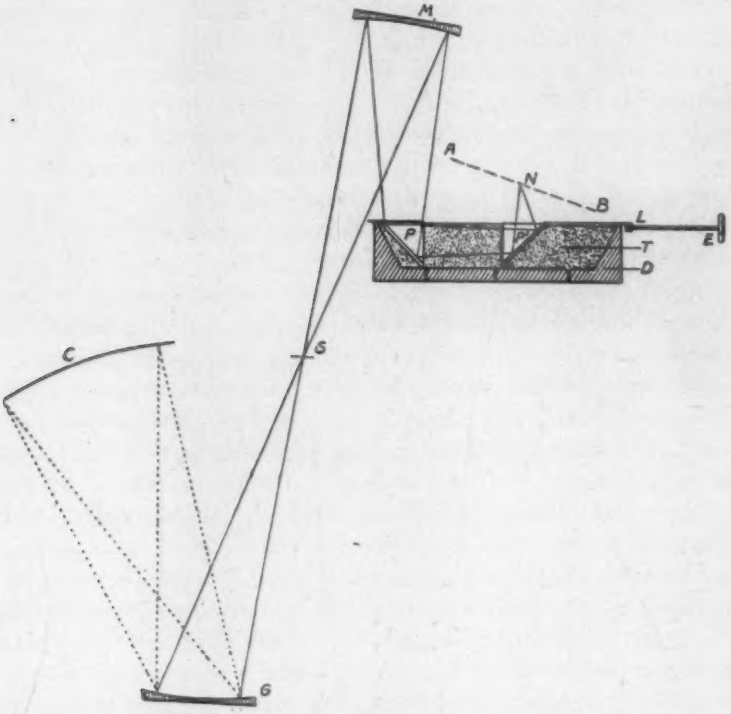
Taking all of the spectroscopic work into account, I regard the evidence from this source as strongly supporting the solvate theory of solution as advanced in this laboratory more than a dozen years ago.

Jones and Strong studied the effect of *rise in temperature* on absorption spectra, both over the range 0° to 100° in open apparatus, and in closed apparatus up to much higher temperatures. The open apparatus is shown in Fig. 9. N is a Nernst glower, arranged to slide along the rod AB. P and P' are quartz prisms which are held by a lid L. The prism P is stationary, whereas the prism P' can be moved by the travelling carriage E back and forth through the trough T, which contains the solution whose absorption spectra is being investigated. AB is so inclined that the optical length of the light beam from N to $P'P$ and the concave mirror M shall be constant, whatever the length of the solution between P and P' may be. The greatest length of path PP' used was 200 mm. The hypothenuse faces of P and P' are backed by air films which are enclosed by glass plates cemented to the quartz prisms.

Considerable difficulty was experienced in finding a cement

that would adhere to the polished quartz prisms at the higher temperatures. For aqueous solutions baked caoutchouc was found to work very well. D is a brass box holding the trough T. D is filled with oil and placed in a water-bath whose temperature can be varied between 0° and 90°. The path of the beam of light is then from the Nernst glower N, or spark, to the quartz

FIG. 9.



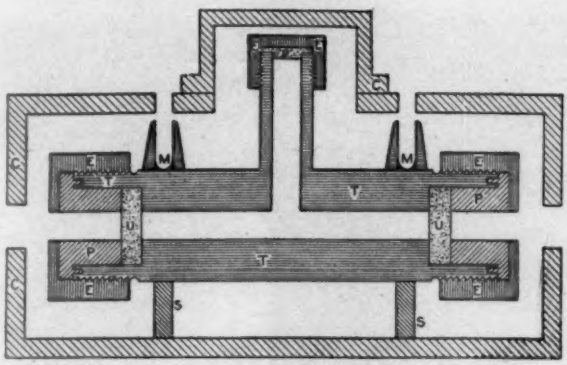
prism P'. The light is totally reflected from the hypothenuse face of this prism through the solution to P. This prism also has its hypothenuse face backed by an air-film, so that the light is totally reflected upward to the concave speculum mirror at M. M_1 focuses the light on the slit of the Rowland concave grating spectroscope, G being the grating and C_1 the focal curve of the spectrum. This prism arrangement was designed by Dr. Anderson. It was found to work very well.

From the study of the effect of temperature on absorption spectra over the range 0° to 90° Jones and Strong concluded that "rise in temperature causes the general absorption of any salt in water to increase, and also causes the bands to broaden and become more intense."

The closed apparatus used by Jones and Strong is shown in Fig. 10.

Two cells, one 1.0 cm. and the other 10 cm. in length, were used. Fig. 10 represents a longitudinal section of the longer cell. Since both cells were exactly alike in all respects except in length and in the size of the side tube, only the longer cell is described here.

FIG. 10.



The main part of the cell (I) was made of tool steel, and was heavily copper plated and gold plated on all the inner surfaces. The side tube was very tightly fitted into the main part of the horizontal tube. The open part of the tube was 1.0 cm. in diameter. The windows of the cell (U, U) were 2.5 cm. in diameter and were either of quartz or glass. One of the troubles with this form of cell is the formation of precipitates on the inside surfaces of the windows. Every time a precipitate is formed the windows have to be taken out and cleaned. On being put back there is always great danger of the quartz or glass ends being broken. During the work a number of ends were broken in this way.

Quartz ends are much tougher and less easily broken than glass ends. They are, however, quite expensive, and in most of the work the solutions were not transparent in the ultraviolet.

For this work glass ends were used. Some of these were cut out of ordinary plate glass, and others were made from "uviole" glass, which is tougher and much more transparent in the ultra-violet than is the ordinary plate glass. For cutting the ends a steel tube 2.5 cm. in diameter was fastened to the axle of an ordinary fan motor in such a way that the tube was vertical, the free end of the steel tube being at the bottom. An old glass end was then cemented to a piece of plate glass with hot sealing wax and served as a guide for the steel tube. The plate glass was then held against the end of the steel tube and the motor started. Wet carborundum was fed constantly against the grinding steel tubes. Plates nearly 1.0 cm. thick could be cut in this way in 20 or 30 minutes.

The quartz windows rested on gold washers which, in turn, rested directly against the gold-plated shoulders of the tube *T*. *P P P* are plungers. Two of these at the ends of the main tube have guide pins that prevent them from turning. Between the plungers and the windows were placed washers. Various kinds of washers of hard leather, lead, zinc, etc., were used. The leather washers, however, seemed to be the most satisfactory. Steel caps, *E E E*, serve to tighten the plungers. *M M* are receptacles for thermometers. *C* is an iron air-bath and prevents rapid changes in temperature in the cells.

In heating a cell of this kind it was found that the rise in temperature must be very gradual. Very great difficulty was encountered in getting the ends to hold liquid-tight. The screw ends were tightened gradually for several days and for several heatings. On one occasion, when the tube was filled with one of the higher alcohols, a very effective closing was made. It is possible that dried films of oils (like linseed oil) might be of use as washers.

This cell worked well in nonaqueous solutions, but water rusted it at the higher temperatures. Another form of cell, to be described later, was used with aqueous solutions at the higher temperatures.

The following spectrogram will show the general character of the results obtained in nonaqueous solvents:

Neodymium Chloride in Methyl Alcohol.—Fig. 11 represents the absorption of a 0.1 normal solution of neodymium chloride

FIG. 11.

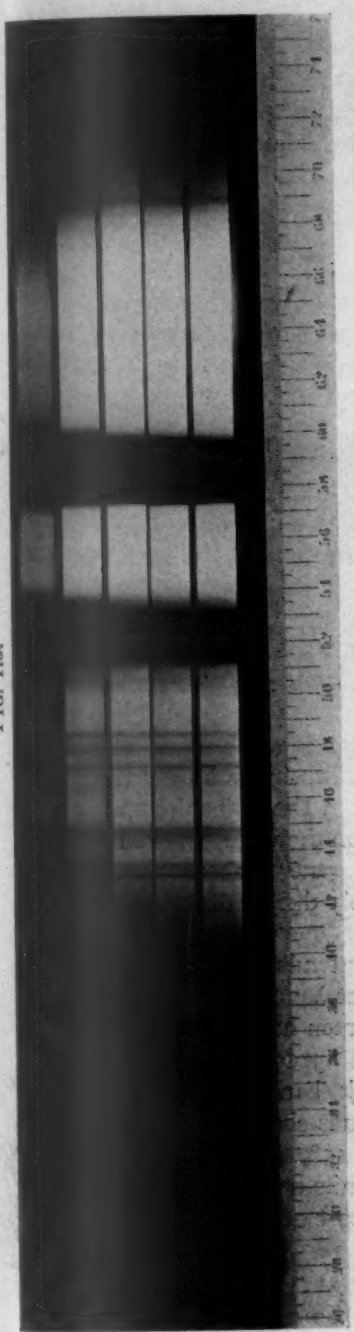


FIG. 11a.

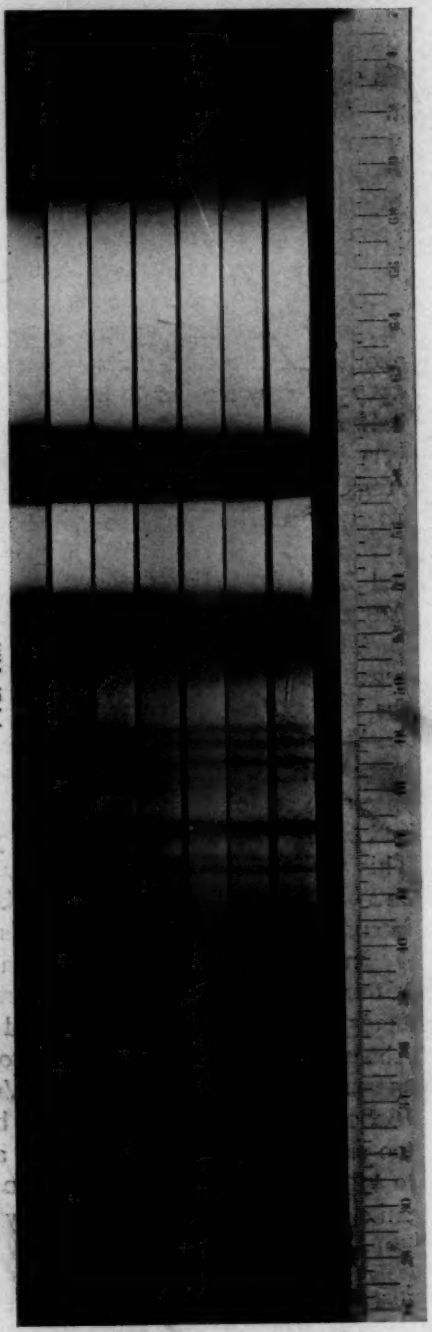


FIG. 11b.

in methyl alcohol, 10 cm. in length. This spectrogram shows the methyl alcohol bands quite sharply. A weak band appears on the first strip λ4015, and at λ4200. The band λ4285 is quite strong and only about 10 Angström units wide. A weak and quite narrow band appears at λ4270. The band λ4270 is rather hazy; λ4450 is about 50 Angström units in width and is very diffuse, its red side not being as diffuse as the violet side. The band λ4620 is very weak, λ4700, λ4770, and λ4820 all have about the same intensity and width; the first two being accompanied by very weak bands on their violet sides at λ4680 and λ4750. The band λ5040 is very weak and broad; λ5120 is about 20 Angström units wide and is very strong. The band λ5175 is very similar to λ5120, except that it is only about one-half as intense. The bands λ5215, λ5250, and λ5290 are all very intense and are quite sharp, the middle band being about 20 Angström units in width, while the other two are only about 10 Angström units wide. There is a wide absorption band from λ5710 to λ5940, with the sharper edge on the violet side. The red band at λ6850 appears to be quite strong and about 20 Angström units in width.

The other strips represent the same solution at different temperatures, these being 15°, 26°, 40°, 55°, and 78°, starting with the lowest strip.

With rise in temperature the bands all become somewhat more intense and wider. The general absorption over the whole spectrum region increases, especially at the higher temperatures, and begins to encroach quite rapidly on the violet and red regions. This violet absorption is probably a general absorption, but the encroaching on the red side is probably due to the increase in the intensity of the group of red bands.

In the upper strip transmission extends from about λ4200 to λ6100. A very weak band appears at λ4200 and another one at λ4305. The bands in the blue and green have changed but little. Absorption is pretty complete from λ5100 to λ5190, λ5210 to λ5350, and λ5690 to λ5990. Weak bands appear at λ6230, λ6280, and λ6750. If any of the bands showed any shift it was too small to measure. The band at 15°, extending from λ5710 to λ5940, widens approximately 20 units on its violet side and 50 units on its red side. It is probably more or less general that wide

absorption bands usually broaden unsymmetrically towards the red, especially when this side is the more diffuse.

A spectrogram representing the absorption of a methyl alcohol solution, 0.2 normal and 1.0 cm. in length, was made. The temperatures were 25°, 40°, 55°, and 70°. The only important change due to temperature was at 70°, the intense absorption near the centre of the ϵ group of bands having practically disappeared.

Neodymium Bromide in Methyl Alcohol.—B, Fig. 11, represents the absorption spectrum of a 0.1 normal solution of neodymium bromide in methyl alcohol. The length of cell was 10 cm. The temperatures were 25°, 35°, 44°, 60°, 82°, 100°, and 120°, beginning with the lowest strip. At the highest temperature a slight precipitate was formed, but still some light was transmitted. The neodymium solutions all become much more deeply colored at the higher temperatures, as can easily be shown by heating such a solution in an ordinary test-tube.

The absorption spectrum of neodymium bromide in methyl alcohol is quite different, so far as minute detail goes, from that of the chloride. In general, the bands of the chloride are from 5 to 15 Angström units farther towards the red than the bromide bands.

For the lowest strip, very weak and diffuse bands appear at about $\lambda 4000$, $\lambda 4180$, $\lambda 4600$, $\lambda 4900$, $\lambda 5040$, $\lambda 5320$, $\lambda 6230$, $\lambda 6260$, $\lambda 6730$, and $\lambda 6790$. The β group of the bromide is very different from that of the chloride. It consists of a very sharp, narrow (3 units) band at $\lambda 4625$, a very sharp and less intense band at $\lambda 4275$, a hazy band at about $\lambda 4280$ which more or less overlaps $\lambda 4275$, and at higher temperatures $\lambda 4275$ cannot be noticed at all. A very weak band appears at $\lambda 4300$, and a broader band, about 20 Angström units in width, at $\lambda 4325$.

The γ group of the chloride is also quite different from that of the bromide, which has four bands of almost equal intensity at $\lambda 4690$, $\lambda 4745$, $\lambda 4765$, and $\lambda 4815$. Weak bands appear at $\lambda 4670$, $\lambda 4700$, and $\lambda 4725$. The δ group consists of a rather narrow band at $\lambda 5090$ and a very strong band at about $\lambda 5115$; a lot of narrow and intense bands at $\lambda 5200$, $\lambda 5220$, $\lambda 5235$, $\lambda 5250$, and $\lambda 5275$ practically merge into a single band. The ϵ group consists of a single wide band extending from $\lambda 5700$ to $\lambda 5880$.

As the temperature is raised the violet increases quite rapidly, and the δ and ε groups of bands become wider and stronger. The later band widens very greatly towards the red. All the bands become very much more diffuse. This is particularly true of the β group, since at 120° only two very hazy, indistinct bands appear; while at 25° some of the bands in this group were almost as fine as spark lines.

No measurable shift of the bands towards the red could be observed.

That the absorption spectra of the chloride and the bromide in methyl alcohol would be so different was quite unexpected, since these two salts have almost identically the same absorption spectra in aqueous solution.

DISCUSSION OF RESULTS OBTAINED BY JONES AND STRONG.

(1) The general effect of rise in temperature is to give a solution of an inorganic salt a deeper color. This deepening of the color signifies that the absorption of light has become more selective, and spectroscopic work indicates that this selective absorption is usually due to a widening of the absorption bands. As these bands are never so distributed over the spectrum as to give a colorless solution, it follows that a widening of the absorption bands will intensify the color of the solution. In many cases this widening appears to be quite unsymmetrical, but this need not necessarily mean that the centre of gravity of the individual absorption band is shifted. Many examples of the neodymium absorption bands show this phenomenon very clearly. For instance, the absorption due to the γ and δ groups of bands may be sufficiently intense to make these groups appear as single bands. If the absorption is not so intense as this, in some solvents it is found that with rise in temperature the shortest wave-length bands may decrease in intensity, and may even disappear. The long wave-length bands increase in intensity, and in some cases new bands appear. Knowing this, it is easy to understand that if the absorption is so strong that each of these groups of bands appears as a single band, these broad bands will widen very unsymmetrically towards the red with rise in temperature. It may be that some change like this takes place in the case of the uranyl bands. It is for this reason that a formula calculated for the widening of

a band with rise in temperature would not apply to many wide bands.

(2) In the case of all pure salts dissolved in a single solvent the bands have been found to widen with rise in temperature, and at the same time they become more diffuse, the edges becoming hazier. When there is a mixture of salts in the same solvent, the bands may become much weaker with rise in temperature. This is the case in a mixture of neodymium and calcium chlorides in water. In a similar manner, the absorption of a salt in two solvents probably decreases in intensity with rise in temperature. An example of this kind is that of uranous bromide in 40 per cent. water and 60 per cent. alcohol. At ordinary temperatures the bands are of about equal intensity. At 80° the water bands have practically disappeared, without the alcohol bands having widened to any great extent.

(3) In general, the centre of intensity of single bands changes but little. Whenever there is any change of wave-length, the shift is invariably towards the red. It seems that this shift is greater the wider the band, so that it is difficult to say in most cases whether the shift is real or only apparent. In the case of solutions of pure neodymium and erbium salts the shift is, in general, too small to be observed.

(4) A study of gaseous aggregates, such as $N_2O_4 \rightleftarrows 2\,NO_2$, indicates that raising the temperature or lowering the pressure increases the relative number of the simpler molecules. Many vapors like those of the fatty acids show molecular clustering at low temperatures. In a similar manner, it would be expected that aggregates would gradually break down at the higher temperatures. In considering specific examples it would be expected that the breaking down of acid uranyl sulphate aggregates would result in a shift of the uranyl bands, the shift being towards the violet. On the other hand, if the nitric acid uranyl nitrate aggregates are broken down, it would be expected that the uranyl bands would be shifted towards the red. Acording to this view, the shift of the uranyl bands of uranyl nitrate in nitric acid and of uranyl sulphate in sulphuric acid, with rise in temperature, should be quite different if the only effect of rise in temperature is a breaking up of the aggregates.

In advancing a hypothesis of this kind it is assumed that it is only the molecules in an aggregate that are effective in changing

the frequency of vibration of the absorbing systems of the light centres. This means that the kinetic energy of the aggregate corresponds to that of a molecule at the same temperature in the solution, the individual molecules in an aggregate all moving together. Whether there is a constant interchange of these molecules and the molecules of the solution, spectroscopic evidence does not as yet show. Neither can it be said with certainty that molecules outside the aggregates do not affect the frequencies of vibration of the absorbing system within the aggregate. Assuming that this is not the case, then it follows of necessity that with rise in temperature the acid aggregates are not broken up, because the uranyl bands of acid solutions are then shifted to the red. This shift seems to be about as great for uranyl sulphate in sulphuric acid as it is for uranyl nitrate in nitric acid. In a similar manner, acid solutions of neodymium salts do not have their absorption spectra changed with rise in temperature so as to resemble more closely that of the neutral salt, as one would expect if the acid neodymium aggregates were broken down.

(5) When foreign salts like calcium chloride are added to solutions of neodymium chloride, it is probable that aggregates containing the two salts are formed. In the case of aqueous solutions of these salts, it is found that the neodymium bands are shifted to the red with rise in temperature, whereas aqueous solutions of pure neodymium chloride do not show this effect at all. Exactly what takes place in this case is not evident.

(6) The effect of rise in temperature on solutions showing the solvate bands of equal intensity, has been to cause a change in the intensity of the solvate bands; very little, if any, change, however, in the wave-lengths of the bands takes place. In the case of water and alcohol, the alcohol bands increase in persistency as the temperature is raised.

(7) In the work with the closed cell at high temperatures, it was found that precipitates were formed in practically every case, probably due to hydrolysis, alcoholysis, etc.; precipitation taking place in dilute as well as in concentrated solutions. Several examples were tested of concentrated solutions of colored salts mixed with calcium or aluminium chloride, and precipitation was found to take place under these conditions at comparatively low temperatures. It would be very interesting to learn whether acid

aggregates of uranyl, neodymium, erbium and such salts are less likely to form precipitates than the neutral salt solutions.

In the case of neutral uranous solutions these precipitates form at 70° or 80°. The presence of acid prevents this precipitation at temperatures below 100°.

Whether the salt precipitation at high temperatures is complete or not cannot be decided in general at present. In the case of several neodymium and erbium solutions this seemed to be the case. In one of the uranyl solutions, however, some uranyl salt remained in the solution after the precipitate had settled.

(8) It may be said, in general, that there is a very great increase in the absorption of all solutions in the short wave-length region of the spectrum as the temperature is raised. How great this increase in absorption would be if pure solutions were used has not yet been determined. The formation of precipitates is usually preceded by a very great increase in the short wave-length absorption.

(9) The problem as to whether a rise in temperature produces a permanent change in the structure of the aggregates in solution has not been studied to any great extent. In the case of the existence of two solvent spectra it is found that the spectra, on cooling the solution, are exactly the same as before heating. In the case of an acetone solution of uranyl chloride it was found that the bands are apparently single after the precipitate was formed during the heating. Whether these bands would have become double again when the solution was cooled was not tested. It would be interesting to learn whether selective solvate precipitation would take place on heating solutions.

Absorption Spectra and the Solvate Theory of Solution.

The first *direct spectroscopic evidence* for the existence of solvates was furnished by Jones and Anderson in their study of salts of neodymium. A salt like neodymium chloride was found to have a very different absorption spectrum in water from what it had in methyl alcohol. Neodymium chloride in the proper mixture of water and methyl alcohol shows both the "water" bands and the "alcohol" bands. By varying the amounts of the solvents relative to one another the relative intensities of the two sets of bands can be changed at will.

Neodymium nitrate in a mixture of water and the alcohol, shows bands of the same character in the two solvents as the chloride.

Praseodymium chloride in a mixture of water and methyl alcohol shows the same kind of change as neodymium chloride. In this case an entirely new band appears in the alcohol, which has no analogue in the aqueous solution.

The existence of " water " bands and " alcohol " bands in the aqueous and alcoholic solutions, respectively, was interpreted by Jones and Anderson as direct evidence for the existence of hydrates in the aqueous solutions and of alcoholates in the alcohol solutions—in a word, is direct spectroscopic evidence for the solvate theory.

The largest amount of, and most direct spectroscopic evidence for the solvate theory of solution has been brought to light by our work, which has been in progress continuously during the past three years. A careful study was made of the absorption spectra of cobalt salts in different solvents and as affected by temperature. Glycerol solutions of these salts showed a different spectrum from aqueous solutions, indicating the presence of glycerolates in such solutions, as we have hydrates in aqueous solutions.

The effect of rise in temperature is to increase enormously the absorption of concentrated aqueous solutions of cobalt chloride, especially in the red. It is well known that such solutions turn blue on heating. The more concentrated the solution the lower the temperature at which this color change takes place. There is a large amount of evidence which points to the conclusion that this change in absorption is due to a breaking down of the more complex hydrates with rise in temperature. If this is the true explanation of the phenomenon, the presence of a dehydrating agent such as calcium chloride or aluminium chloride ought to cause this change in absorption to take place at a lower temperature, since the dehydrating agent would assist the rise in temperature in breaking down the complex hydrates.

The results here are in accord with prediction. The addition of either of the above chlorides causes the great absorption in the red to take place in more dilute solutions at the same temperature, or in a given solution at a lower temperature.

It was further found that the temperature at which this marked change in the red absorption takes place is higher for aqueous and glycerol solutions than for solutions in other solvents,

showing that the "hydrates" and "glycerolates" are more stable with respect to temperature than other solvates.

The effect of rise in temperature on salts of chromium was also studied, and was shown to be similar to the effect of rise in temperature on cobalt salts—the higher the temperature the greater the absorption.

WORK OF JONES AND GUY.

Jones and Guy studied the effect of high temperature on the absorption spectra of solutions, using the following form of apparatus devised by Strong.

The reason that the work of Jones and Strong was not pushed to higher temperatures, with aqueous solutions, was that the form of apparatus then in use did not admit of it. This consisted of a steel tube,[52] lined on the inside with copper and plated with gold on all of the inner surfaces. This worked very satisfactorily with nonaqueous solutions, the gold plate adhering firmly to the copper, which, in turn, remained adherent to the steel.

When an aqueous solution was heated in the apparatus from 100° to 200° the result was unsatisfactory. The water, under the high pressure, forced its way through the copper and the gold and rusted the iron, as has already been stated. The result was that the copper with the gold, separated from the steel, and the solutions, after heating for a time, gave the iron reaction. This apparatus had the further disadvantage that when a precipitate formed with rising temperature it was necessary to open the entire apparatus and remove the glass ends in order to clean them.

To overcome these difficulties the following form of apparatus (Fig. 12) was constructed by Strong, and used to study the effect of rising temperature on the absorption spectra of aqueous solutions.

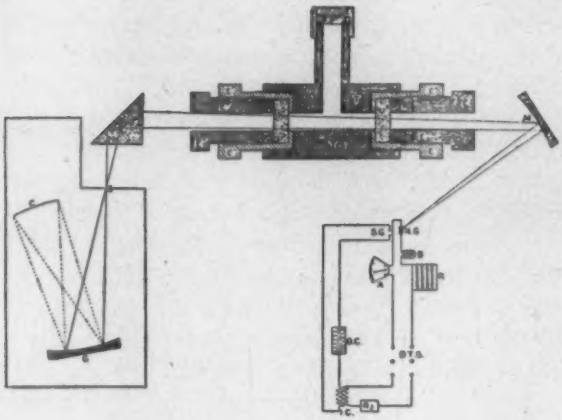
The quartz ends are fastened into the ends E'. The plunger P has guide grooves instead of guide pins. A part of the plunger is provided with screw threads for removing it. The entire cap is removed from tube T by unscrewing E', during which the quartz end is untouched. When the ends are removed the quartz window can be easily cleaned. Gold washers were inserted between T and E' and between E' and U.

The general arrangement of the apparatus is also shown in

[52] *Amer. Chem. Journ.*, 47, 30 (1912).

Fig. 12. The cell is kept in a horizontal position so that any bubbles that may form will rise in the side tube. The spectroscope, containing the grating *G*, photographic plate holder *C*, and slit *S*, being kept vertically, a 45° quartz prism was used to change the horizontal beam of light into a vertical beam; the beam being totally reflected by the hypothenuse surface of *O*. The source of light *N G* (Nernst glower) or *S G* (spark gap) was focused by the concave speculum mirror *M* on the slit *S*. A similar arrangement was used for the fused silica cell. *D T S* is a double-

FIG. 12.



throw switch, by means of which either the Nernst glower or the spark gap may be thrown in circuit. *B* is a ballast. *R* is a variable resistance, by means of which the current in the Nernst glower, as shown by the ammeter *A*, may be kept constant. *O C* is an oil condenser. *I C* is an *X*-ray induction coil, and R_2 is a resistance in the primary circuit of this coil.

One spectrogram will give an idea of the general character of the results obtained.

Neodymium Chloride in Water (*see Fig. 13*).

The solution whose spectrum is given in Section A was saturated, the depth of absorbing layer being 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 140°, and 165°, respectively.

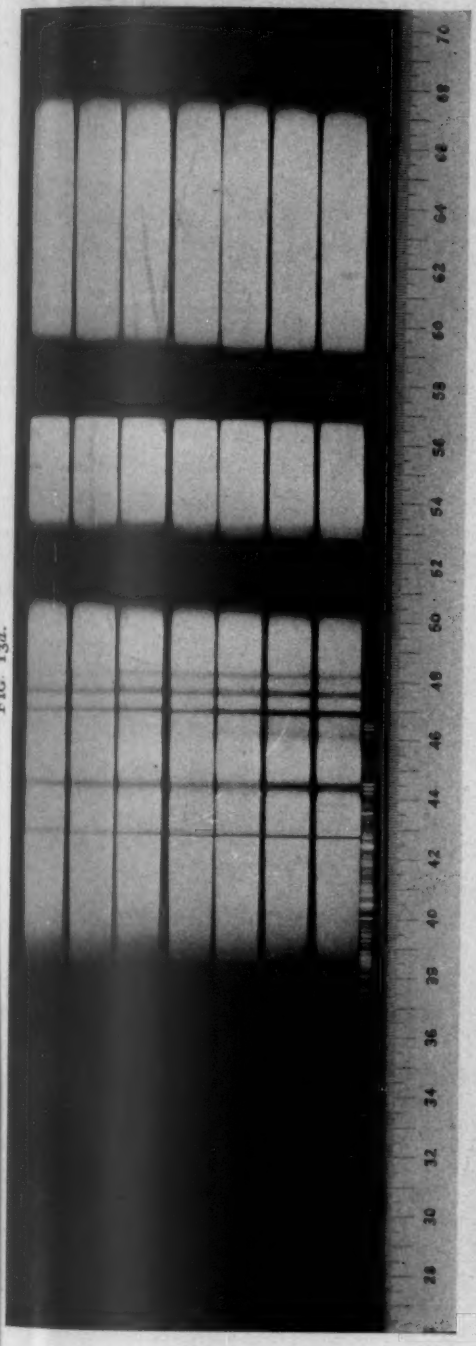


FIG. 13a.

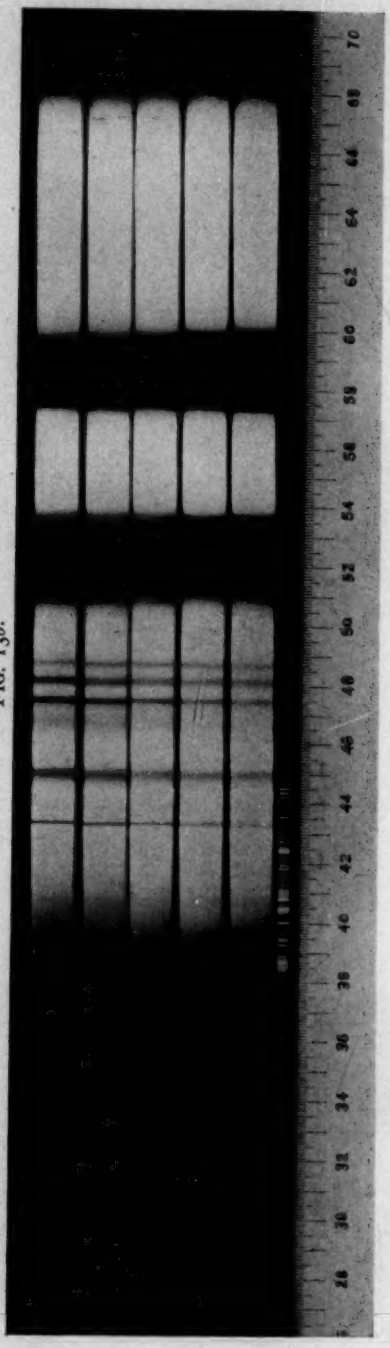


FIG. 13b.

Absorption bands which are unchanged by the range of temperature from 20° to 200° appear at $\lambda 3800$, $\lambda 4025$, $\lambda 4200$, $\lambda 4325$, $\lambda 4440$, $\lambda 4600$, $\lambda 4690$, $\lambda 4750$, and $\lambda 4820$.

The double band from $\lambda 5050$ to $\lambda 5270$ is only slightly affected, if at all.

The two most interesting absorption bands are those whose centres are near $\lambda 4275$ and $\lambda 5800$. The former of these in strip 1 is very sharp and intense, though only a few Angström units wide. Both edges were well defined. As the temperature is raised the violet edge remains very sharp, while a rapid shading off of the red edge takes place. At a glance the band appears to be less intense in the higher temperature strips, but on close examination it is seen to be more diffuse; the red edge diffusing over a range of about 20 Angström units at the highest temperature. This is exactly in accord with what Jones and Anderson [53] had found. They showed that when the number of molecules in the path of the light was kept constant, this band remained practically constant; while it had been shown by Jones and Anderson and by ourselves, that this band changes with dilution, being more intense in the most concentrated solution.

The $\lambda 5800$ band is affected most by temperature as well as by dilution. In strip 1 this band is about 200 Angström units wide, and increases regularly in width as the temperature is raised, until at the highest temperature the width is over 250 Angström units; or there is a total widening of 50 Angström units. The violet edge remains perfectly sharp, while the shading is towards the red end of the spectrum.

It occurred to us that whatever effect might be produced by rise in temperature, if it was a true temperature effect the reverse should happen when the solution was allowed to cool.

With this in view B was made. The concentration of the solution and the depth of layer photographed in Section B were exactly the same as in A. In fact, the identical solution was used. As soon as the film A had been exposed with rising temperature, it was removed from the camera and developed. Without even allowing the cell to cool, another film was placed in the camera and Section B made with falling temperature. In B the temperatures were 165°, 140°, 115°, 95°, and 70°, the highest temperature being nearest the numbered scale.

[53] Carnegie Institution of Washington, Publication 110.

A study of the original film shows changes only in bands $\lambda 4275$ and $\lambda 5800$; and this change is exactly the reverse of that shown by these same bands in A. The $\lambda 4275$ band appears in strip 1 with a sharp violet edge, and shading off towards the red over a range of 15 or 20 Angström units. As we pass to the succeeding strips in the direction of falling temperature, the red edge becomes sharper and sharper until, in strip 5, which represents the lowest temperature, the band assumes its normal sharp edge on the red side and covers less than ten Angström units. The $\lambda 5800$ band narrows uniformly from the red end, as the temperature falls, the total narrowing being about 40 Angström units.

THE EFFECT OF DILUTION ON THE ABSORPTION OF LIGHT BY SOLUTIONS.

The question as to the effect of dilution on the power of solutions to absorb light is an old one. This question became especially prominent at the time the theory of electrolytic dissociation was proposed. In dilute solutions of electrolytes there are practically only ions present, very few molecules existing as such. All of the properties of such solutions are the properties of the ions contained in them. Therefore, the power of these solutions to absorb light must be due to the ions present in them. This was the reasoning in vogue, and the conclusion drawn.

It was at the same time freely recognized that molecules in solution have the power to absorb light. This was shown by the fact that solutions of non-electrolytes, or completely unionized substances, are often colored; and color in solution means selective absorption of light.

The result of the conclusion drawn from the theory of electrolytic dissociation, was that an enormous amount of work was done on the absorption spectra of dilute solutions of both electrolytes and non-electrolytes. Ostwald carried out an elaborate investigation on the relation between color and dissociation, and published the work under the title "Ueber die Farbe der Ionen."[54] A large number of salts were brought within the scope of this investigation. Salts of an acid having a colored anion, with colorless cations were studied. This is illustrated by the various permanganates, hydrogen, sodium, ammonium, magnesium, zinc, cad-

[54] *Zeit physik. Chem.*, 9, 579 (1892).

mium, etc. Ostwald showed that these salts of any given acid had essentially the same spectra. In a similar manner, he studied salts of fluorescein, eosin, iodoeosin, resolic acid, diazoresorcinol, etc. Ostwald then reversed the process and compared the salts of a given colored base with colorless acids. Thus, he studied the salts of *p*-rosaniline with acetic, chloric, benzoic, hydrochloric, nitric, butyric, salicylic, lactic, etc., acids, and found practically the same absorption spectra for all of these salts.

From the standpoint from which he undertook his investigation, Ostwald may be said to have solved the problem of the rôle of ions in the absorption of light, so far as that could be done with the prism spectroscope.

The problem that we studied was of a different nature. It had to do with the absorption spectra of ions relative to that of the molecules from which they were formed. Some earlier work of Jones and Anderson [55] had shown that if molecules have different action on light from ions, the difference is slight; indeed, so slight that there would be no hope of detecting it by ordinary means, even with a grating spectroscope. This problem was attacked in the following manner:

Making a Dilution Spectrogram.

Before entering upon a detailed discussion of the spectrograms it is wise to state briefly the method used in making any given spectrogram. Throughout all the work done on the effect of high dilution on absorption spectra, under the conditions of Beer's law, only three exposures were made for any given spectrogram, —*i.e.*, only three dilutions were compared. The depths of cell in all cases were 0.5 cm., 50 cm., and 250 cm., the dilution being increased one hundred times between the first two solutions and five times between the last two; or a total dilution of five hundred times between the first and last solution. Smaller depths of cell than 5 mm. were not used, on account of the large percentage error in measuring such depths.

Much difficulty was experienced in getting sufficient light through the longer cells to fill the grating completely, nor was this possible unless the tube containing the solution was constantly

[55] Carnegie Institution of Washington, Publication 110.

moved backward and forward so that the image of the source of light was moved along the slit of the camera.

By such a procedure the surface of the grating could be illuminated fairly uniformly, and the exposures gave good results on the photographic plate, as is shown by the spectrograms.

In order to insure complete illumination of the grating a uniform procedure was adopted. The longest cell, containing the most dilute solution, was first placed in position; the light passed through, and the image of the Nernst glower sharply focused on the slit of the camera in such a manner as to throw as much light as possible on the grating. By holding the eye in the position later to be occupied by the photographic plate, we could easily tell when the grating was properly illuminated.

After everything was satisfactorily adjusted the lights were extinguished and the plate inserted in the camera. Great care was taken not to move any parts of the apparatus; the camera was closed, the source of light again turned on and the exposure made. It is clearly seen that in making any spectrogram, using three cells differing in length so markedly, we virtually had three different sources of light; and, consequently, the length of exposure sufficient to give comparable results on the photographic plate had to be determined by a long series of experiments. In the case of the longest cell, exposures as long as several minutes were made; while with the shortest cell only a few seconds were necessary to give good, clear spectrograms on the photographic plate.

The remaining procedure was essentially the same as that described by Jones and Anderson [56] and by other workers in this laboratory.

One plate will show the character of the results obtained.

Neodymium Chloride in Water (see Fig. 14).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the spark spectrum, were 2.05, 0.0205, and 0.00401 normal, respectively; the corresponding depths of absorbing layer being 0.5 cm., 50 cm., and 250 cm.

For B the concentrations used were 1.025, 0.01025, and 0.00205 normal. The depths of layer were the same as used

[56] Carnegie Institution of Washington, Publication 110.

FIG. 14*a*.

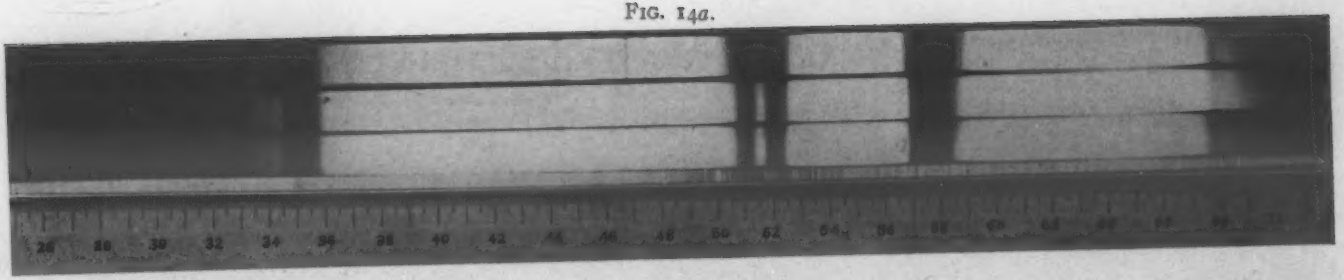


FIG 14*b*.

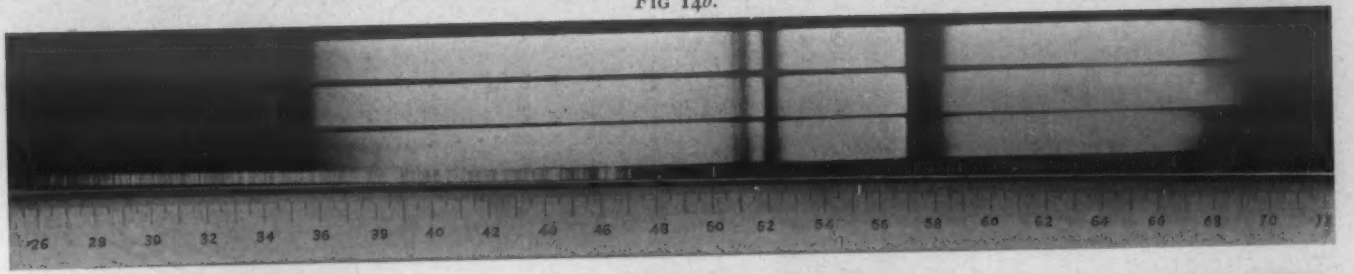
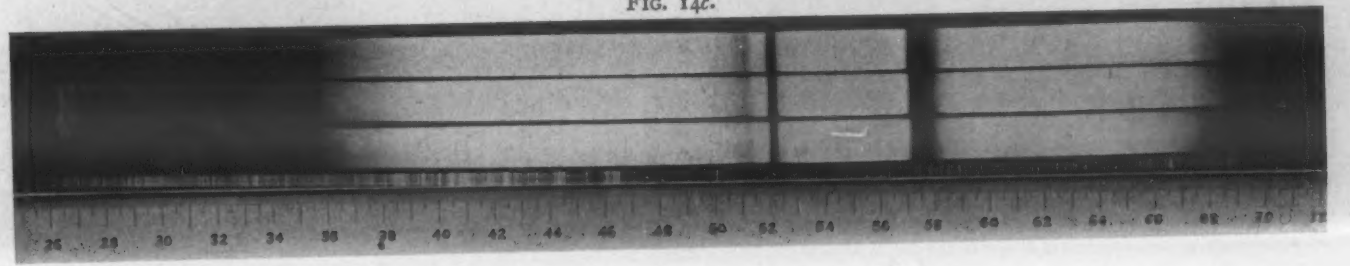


FIG. 14*c*.



in A. It is seen that the dilutions are just one-half that of the corresponding layers in A.

The concentrations of solutions used in making C were just half of those in B,—*i.e.*, 0.512, 0.00512, and 0.00102 normal. In the entire plate, as in the dilution work, the most dilute solution is always nearest the spark spectrum.

Since very much of the finer detail, and several of the narrowest bands are lost in reproducing and printing the films, our discussion is always based upon the original photographic film. Lines will frequently be discussed which do not appear on the printed plates, but which are very clear and distinct on the photographic film.

A study of A shows complete absorption in the violet up to λ3350; then slight transmission for about 50 Angström units. The faint hazy band λ3400, and the well-defined band λ3450–λ3600 are not affected by the change in dilution. Hazy bands appear at λ3820, λ4040, and λ4200. Their intensities do not seem to be affected by dilution. The beautiful sharp band λ4275, is slightly more intense in the most concentrated solution. The effect of dilution, if any, on the bands λ4325, λ4440, λ4600, λ4690, λ4750, and λ4820 is not measurable. On the original film they appear slightly broader, but not more intense, on the third strip.

Bands which have their centres near λ5100, λ5200, and λ5800 are decidedly affected by dilution; the former two appearing distinctly as independent bands in the most dilute solution, diffuse with a single broad band with the centre near λ5150. There is the greatest change between the second and third strips (in discussing any plate strip 1 is always nearest the spark lines). The broadening of these bands, both of which have rather hazy edges, is fairly uniform,—*i.e.*, they widen both towards the red and violet ends of the spectrum.

The intense band which extends from λ5690 to λ5850 is affected very markedly by dilution, the widening being almost entirely towards the red end of the spectrum. The violet edge is hardly affected, while the widening towards the red is about 50 Angström units. Here also the change in the width of the band is greatest where the change in concentration of the solution is greatest. There is a very faint band, λ6225, which appears slightly more diffuse in the most concentrated solution.

The concentrations of the solutions used in B, are just one-half those of A, and it is seen that some of the smaller bands are lost, while the broader ones have split into two or more smaller bands. In this film bands near λ3425, λ3475, λ3520, λ3575, λ4275, λ4340, λ4450, λ4700, λ4750, λ4820, λ5100, λ5120, show no change with dilution. The broad band λ5700–λ5825 shows a widening of about 25 Angström units, being the only band which is changed by dilution.

C of this plate is the spectrogram of solutions twice as dilute as those of B. No band on this plate shows any appreciable change produced by dilution, except probably a slight widening of λ5750.

We then see, from a study of this plate, that in A, bands λ4270, λ5100, λ5200, and λ5750, narrow with dilution, the amount of change being in the order given; that is, least in λ5100 and greatest in λ5700. In B there is an appreciable change in only λ5750, while in C none of the bands are affected by dilution.

Only the two bands λ5275 and λ5800 show marked change with rise in temperature. There is a general tendency for almost all the other bands to become slightly more diffuse, although it is difficult to say that this may not be caused by general absorption. However, with bands λ4275 and λ5800 the change is a real one. Experiments made by overexposing the strips corresponding to the high temperatures, had little or no effect on the changes produced by raising the temperature. Since the development of a photographic plate depends upon the amount of light falling upon it, independent of the period of time it is falling, it is clear that the effect of general absorption could be counterbalanced by increased time of exposure.

The two bands mentioned above widened rapidly as the temperature was raised, this widening being, in both cases, almost entirely towards the longer wave-lengths.

The band λ5800, in the most concentrated solutions, widened as much as 80 Angström units; while the amount of widening was directly dependent upon the concentration. It is always greater between the second and third strips. This is what we should expect, since the change in dilution between the two solutions whose spectrogram they represent, is one hundred times, while the succeeding dilution was only five times. The violet edge

of this band remains almost constant over the range of temperature studied.

The band λ4275, a very sharp, intense band at the lower temperatures, becomes rapidly diffuse as the temperature of any solution is raised. With this band, as with the λ5800 band just discussed, the change is taking place almost exclusively on the red edge; the shading being a gradual one. This edge, the definition of which at ordinary temperature could be seen almost to 1 Angström unit, covers about 40 Angström units at 190°. The double band with its centre near λ5150 remains about constant in any given section; but in those bands whose width or intensity is changed by change in temperature, the change is greatest in the most concentrated solutions,—*i.e.*, where the number of molecules is greatest.

It has been shown that with dilution three of the neodymium bands are affected, namely, λ4275, λ5150, and λ5800. Of these three the change is apparently greatest in λ5800, next in λ5150, and least in λ4275. It cannot be said to be really least in λ4275, but rather less noticeable. It is probable that the percentage change, with regard to the total width of the band, is much greater with this band than in the two preceding bands.

The change in λ5800 is a widening of about 60 Angström units in the most concentrated solutions, as we pass in the direction of the concentrated solutions. This widening, as in the temperature effect, is entirely towards the red end of the spectrum. The widening of the double band near λ5150 is uniform toward both ends of the spectrum. This change is appreciable only in the very concentrated solutions.

Considering a single plate, which represents the spectrogram of three different dilutions in terms of Beer's law, we see the following:

This change is greatest in Section A,—*i.e.*, the most concentrated solution; less in B; and hardly measurable in C.

The change is greater with the acetate than with the other salts of neodymium, and is always greatest where the difference in concentration is greatest,—*i.e.*, between strips 2 and 3.

When we consider the effect of dilution on the dissociation, we see it is in this same ratio;—*i.e.*, there is a much greater percentage change in the relative number of molecules pres-

ent in concentrated than in dilute solutions, for a given change in dilution.

In that dilution of any solution where the relative number of molecules is greatest—the association greatest—bands $\lambda 4275$, $\lambda 5150$, and $\lambda 5800$ are widest, and the change in dilution which affects the relative number of molecules to the greatest extent, causes the greatest change in the bands. In the more dilute solutions where this change in the number of molecules is small, there is a relatively small change in the width or intensity of the bands.

A rise in temperature produces the same change upon bands $\lambda 4275$ and $\lambda 5800$ as concentrating the solution,—that is, rise in temperature and dilution produce the reverse effect. Band $\lambda 5100$ is changed by dilution and not by temperature. From these facts it seems that band $\lambda 5100$ may be associated with the molecules themselves, while bands $\lambda 4175$ and $\lambda 5800$ have more to do with the hydrated molecule. A rise in temperature would make the hydrated absorbers, or the hydrated system containing the absorbers, simpler; and, therefore, probably freer to respond in resonance to a larger number of wave-lengths. This would cause a widening of the absorption bands. Concentrating the solution, —*i.e.*, decreasing the actual amount of solvent,—would, according to the mass law, decrease the amount of solution; and, hence, have the same effect as raising the temperature. This is exactly what is shown to be the case by the plates with bands $\lambda 4275$ and $\lambda 5800$.

The $\lambda 5100$ band is not appreciably affected by temperature, but is changed by dilution, being widest in the most concentrated solutions.

Since temperature has little or no effect on this band, it is probable that here hydration plays very little part. Since the band widens as the number of molecules is increased, it seems to be in some way associated with the unhydrated molecules.

So far as can be seen from the photographic plates, the other neodymium bands are affected neither by dilution nor by temperature. The absorbers in this case are probably associated with the neodymium atoms or ions.

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER—NEW EVIDENCE FOR THE SOLVATE THEORY OF SOLUTION.

The radiomicrometer is simply a thermo-element attached to a loop of thin copper wire suspended in a magnetic field. One of the greatest difficulties in constructing this element is to obtain copper wire which is free from all magnetic metals. If perfectly pure copper wire could be found, an instrument could be constructed of almost any desired sensibility.

A very good specimen of small copper wire was furnished us by Leeds & Northrup, of Philadelphia. This wire was dipped in dilute nitric acid, and the exterior dissolved away until the wire was of proper size. The removal of the outside coating of the wire removed practically all of the magnetic material from it, this material probably being iron from the dies through which the wire was drawn.

It was not a simple matter to construct a satisfactory thermo-electric junction. The alloys used in making this junction were 90 parts bismuth and 10 parts tin, and 97 parts bismuth and 3 parts antimony. The method of making the thermo-electric junction, and of soldering it on to the ends of the loop of copper wire, we owe to Prof. A. H. Pfund.[57] Fine strips of the alloys were obtained in the following manner:

A few grammes of the alloy in question were fused in a vessel free from all magnetic material, and then thrown tangentially upon a clean and smooth glass plate. In this way strips of the metal were obtained of almost any desired thickness. Some were too thin to handle; those used being about 1 mm. wide, 0.01 mm. thick, and about 5 mm. in length.

The thermo-element was made by soldering an end of a strip of one of the above-named alloys to an end of a strip of the other, the whole having the form of a letter V. The two free ends of the V were soldered to the two ends of the loop of copper wire. The soldered surfaces were blackened to absorb the energy more completely. At the end of the loop of copper wire opposite the thermo-element, a light glass rod is fastened. This carries the mirror and is suspended from above by a quartz

[57] *Physic. Rev.*, 34, 228 (1912); *Physik. Zeit.*, 13, 870 (1912).

fibre. The mirror employed was about 4 square mm. This entire system, consisting of thermo-element, loop of copper wire and mirror, weighed about twenty milligrammes. It was suspended by means of a quartz fibre so that the loop hung between the poles of a strong magnet. This entire system was suspended in the interior of a glass tube, the tube being closed by a ground glass stopper, and provided with suitable windows for exposing the junction and observing the mirror. The upright tube was provided with a side tube for evacuation, and by a method devised by Professor Pfund a very high vacuum could be obtained and maintained for any desired length of time. By suitably turning the ground-glass stopper in the top of the glass tube, the loop of copper wire, mirror, and, indeed, the whole system could be made to occupy any position relative to the magnets, even after the entire system had been evacuated. The whole apparatus was supported upon a levelling stand, and packed in cotton to protect it from external radiation, the thermal junction alone being exposed to the radiation in question.

The sensibility of the instrument used can be seen from the following data: It had a full period of 8 seconds; and with a candle at a distance of a metre gave a deflection of 15 cm., when the light was allowed to fall on the junction after passing through a glass window.

When the apparatus was pumped out and the radiomicrometer thus suspended in a vacuum, the deflection for a candle at a distance of a metre was 50 cm. Since glass absorbs just about half the energy emitted by a candle, our radiomicrometer, when provided with a rocket-salt window and exposed to a candle at a distance of a metre, would give a deflection of about 100 cm.

The use of the radiomicrometer in studying the absorption spectra of certain substances has already been discussed by Jones and Guy.[58] The radiomicrometer was used in the study of absorption spectra of solutions, rather than the grating spectrograph and the photographic plate; because the radiomicrometer enabled us to measure not only the positions of the different lines and bands, but also to study quantitatively their intensities. Further, the radiomicrometer, as has already been pointed out, enables us to study the absorption spectra of solutions over a much greater range of wave-lengths than the photographic method.

[58] *Physik Zeit.*, 13, 649 (1912).

In building a radiomicrometer that would be adapted to this work,—that is, with sufficient sensibility and with a short period,—one of the greatest difficulties encountered was to obtain copper wire free from iron. This was a necessity, since the presence of an appreciable quantity of iron in the copper gave rise to a "magnetic control" which rendered the instrument unstable and the zero point inconstant. This difficulty was for the most part overcome, due to the kindness of Messrs. Leeds & Northrup, of Philadelphia, and of R. W. Paul, of London. They both furnished us with copper wire so free from iron that the "magnetic control" could easily be regulated. By means of this wire and the thermo-electric junction already described,[59] a most sensitive radiomicrometer, which at the same time had a very short period, was built. Work with salts of neodymium and praseodymium, the results of which were recorded in the *Physikalische Zeitschrift,* was done with this instrument.

At the beginning of the academic year 1912–1913 the absorption spectra of solutions of a large number of salts of different metals were mapped out. The spectra of these salts were compared with the absorption of water, using the same depths of water as the water in the various solutions. It was soon found that the absorption of the solution was *less,* and in some cases *very much less* than that of the layer of water having a depth equal to the depth of the water in the solution. The depth of water in the solution was determined from the concentration of the solution and from its specific gravity.

It is obvious that the above is a very remarkable fact. The dissolved substance could not have less than no absorption of light; the assumption having been made, up to this time, that in an aqueous solution the water present absorbs just as much as pure, uncombined water. The above result is directly at variance with everything that was known at the time.

It became at once obvious that we could not measure the absorption spectrum of a solution, subtract from it the absorption due to water, and conclude that the remainder was the absorption due to the dissolved substance; since the water in the solution has very different absorption from an equal amount of pure, uncombined water.

We then carried out a number of experiments in cells whose

[59] *Physik. Zeit.,* 13, 651 (1912).

depths could be easily and accurately adjusted, with different substances, in the following manner: We measured the absorption spectra of a number of different substances. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent. The percentage transmission,—that is, the deflection of the radiomicrometer for the solution, divided by the deflection for water,—for the first-named substances, amounted to more than one hundred per cent. Pure water had a different absorption from an equal depth of water in the solution, and, since this difference varied from one dissolved substance to another, it is obvious that this method was not the one to be followed. It would be very difficult, not to say impossible, to interpret the results obtained by dividing the radiomicrometer deflection for the solution by those for pure water. We should simply be obtaining the transmission of the solution in terms of pure water, which was not what was desired.

What we want to know is the actual absorption or transmission of the solution, and then that of pure water having a depth of layer that was just equal to that of the water in the solution. These two sets of results could then be compared with one another.

In this earlier work we had, however, noted that solutions of those substances which are largely hydrated, are more transparent than pure water having the depths of the water in the solutions in question. Solutions of non-hydrated substances, or of only slightly hydrated substances, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution.

It would seem from this observation that water combined with the dissolved substance had less absorption of light than pure, uncombined water. To test this quantitatively the following procedure was adopted:

A solution of the substance in question was prepared of known concentration and its specific gravity determined. This solution was placed in one cell, set to a depth of say 2 mm. Some of the same solution was then placed in another cell, set to a depth of say 1 mm. Light of given, known wave-length was then passed through

the one solution and the deflection noted. Light of this same wave-length was then passed through the other solution, and the deflection in this case also noted. The deflection produced when the deeper solution was in the path of the beam of light was then divided by the deflection produced when the shallower solution was in the path of the light, and this gave the absolute transmission of the solution of the substance in question of known concentration, having a depth of layer of 20 mm. This process was repeated for the different parts of the spectrum, changing the wave-length of light from reading to reading by only a small amount. Light of any given wave-length was always passed through the one solution, and then, at once, through the other solution of a different depth. The object in using the two depths of the same solution, and then dividing the deflection produced by the deeper layer by that obtained when the more shallow layer was in the path of the beam of light, was to eliminate any effect of reflection from the glass ends closing the cells containing the solutions, and also to eliminate any changes in the total amounts of energy sent through the solution, due to slight changes in the intensity of the Nernst glower.

From the specific gravity of the solution and its known concentration, the amount of water in a layer of the solution, say 21 cm. in depth, could easily be calculated. Similarly, the amount of water in a layer of the solution which was 1 mm. deep could also be calculated. Water was then introduced into the two cells, and these cells so adjusted that the difference in the depth of the two was exactly equal to the depth of the water in the layer of the solution which was 20 mm. deep.

The deflection for the water in the deeper cell was then read for any given wave-length of light; and then, at once, the deflection when the light was passed through the *more shallow* layer of water. The deflection for the deeper layer was divided by the deflection for the more shallow layer. This operation was repeated for the various wave-lengths of light in the manner just described. The result was the absolute transmission for water with a depth of layer just equal to the depth of water in the solution in question.

The above results for the solution are plotted as one curve, and those for water having the same depth as the water in the solution as another curve, wave-lengths being abscissæ and

transmission ordinates. A comparison of the two curves shows at once whether water in the free, uncombined condition, or the same depth of water in the solution in question is the more transparent.

The data obtained by dividing the deflections produced by the deeper solutions by those for the more shallow, and, similarly, by those for water, are also given in the following tables. These are the data from which the accompanying curves were plotted.

The substances studied were chosen from the standpoint of their power to solvate or to combine with the solvent in which they were dissolved. In all of the work recorded in this paper the solvent used was water. We were practically limited, in this phase of the work, to those substances which themselves have little or no power to absorb light. We were limited to those substances that are both colorless in the visible part of the spectrum, and have little or no absorption in the regions in which the absorption bands of water occur.

We selected for these substances with little or no hydrating power salts of potassium and ammonium. The potassium salts studied were the chloride and nitrate. Ammonium chloride and nitrate were also investigated. We selected for the salts with large hydrating power calcium chloride, magnesium chloride, and aluminium sulphate. These salts were shown by the earlier work in this laboratory, which was done shortly after Jones proposed the solvate theory of solutions, using the freezing-point method, to be among the most strongly hydrated substances with which we are familiar.

It will be seen from the following data that two depths of layer of each solution of every substance investigated were employed. The object of this was to bring out the two most important water-bands in the region of the spectrum investigated. This could not be done by studying only one depth of solution, since the depth which was necessary and sufficient to bring out clearly one of these water-bands, would not bring the other out in the way desired. By using the two depths of solution and studying each of them in the manner described above,—that is, by the differential method,—we were able to investigate both of the water-bands as produced, on the one hand, by the pure solvent, and, on the other, by the solution.

(*To be continued*)

THE CHEMISTRY OF HUMUS, WITH SPECIAL REFERENCE TO THE RELATION OF HUMUS TO THE SOIL AND TO THE PLANT.*

BY

S. L. JODIDI, B.S., Ph.D.

[This article is largely based upon the work conducted during the last six years by the writer while he was connected with the Michigan and Iowa Agricultural Experiment Stations.]

UP to a few years ago the generally-accepted idea was that humus is made up of but a few organic compounds, chiefly acid in their nature. However, the more recent investigations have thrown enough light upon the chemical nature of humus or humus organic matter in the soil to demonstrate that it is a very complex substance which, in addition to the dark-colored humin bodies, contains a large number of organic compounds displaying acid, basic, neutral, and amphoteric character.

Considered from a modern point of view, the solution of the humus problem consists, first of all, in finding out all of the compounds—the simple bricks—of which humus is made up, as well as the proportion in which those compounds are mostly present in humus, and, further, to ascertain just which of the compounds in question are, as such, present in humus and which of them constitute parts of one or several more complex bodies.

What we at present designate as soil organic matter or humus will thus, in the course of time, by modern methods of research, be separated into a number of bodies of well-known composition and structure.

Whereas a part of the above problems may now be considered as accomplished—the results in question will be mentioned later—it may be worth while to show here that in some measure the development of the idea of the chemical nature of humus stands in a certain relation to the development of the chemistry of carbohydrates and proteins out of which humus is being formed in the soil.

For centuries mankind knew only cane-sugar or saccharose, which was originally extracted exclusively from the sugar-cane. The same sugar was later discovered in the sugar beet (Marg-

* Communicated by the author and published by permission of the Secretary of Agriculture.

graf, 1747), sorghum, maple tree, and other plants. In addition to this sugar, there were discovered, also, lactose in the milk (Bartoletti, 1619), glucose (Lowitz, 1792), fructose (Dubrunfaut, 1847), etc., so that at present we know a considerable number of sugars in the form of bioses, trioses, tetroses, etc., up to nonoses,—*i.e.*, sugars which contain in their molecule from two to nine carbon atoms respectively, and which in part occur as such in nature, the pentoses and hexoses and the corresponding polysaccharides being the most important ones.

As was demonstrated by many researchers, such sugars and, generally speaking, carbohydrates,[1] when treated with acids or alkalies, yield brown or black humin substances, whose physical and chemical properties remind one of soil humus to such a degree that the artificial and natural products were considered by some as closely related,[2] by others even as identical.

When, however, dilute acids are applied, the carbohydrates yield a number of well-defined intermediary products. Thus the polysaccharides furnish, first, monosaccharides; these latter yield organic acids, etc. For the raffinose,[3] *e.g.*, we have: Raffinose (melitriose) → melibiose (+ d-fructose) → d-glucose + galactose. The monosaccharides obtained can yield, *e.g.*, lactic[4] acid, butyric[5] acid, alcohol,[6] citric acid, etc., depending upon the conditions of fermentation.

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[1] Malaguti, *Ann.* (Liebig), vol. 17, p. 52 (1836); Berzelius, "Lehrbuch d. Chemie," 3. Aufl., 1839, 8. Bd.; Conrad u. Guthzeit, *Ber. d. chem. Ges.*, vol. 18, p. 439 (1885), vol. 19, p. 2850 (1886); Sestini, *Gaz. Chim. It.*, vol. 10, pp. 121, 355; Grote u. Tollens, *Ann.* (Liebig), vol. 176, p. 181 (1875), vol. 202, p. 226 (1880); Péligot, *Ann. Chim. Phys.* [2], vol. 73, p. 208; Mulder, *Ann.* (Liebig), vol. 36, p. 243, Chemie der Ackerkrume; O. Schmiedeberg, *Arch. expt. Path. und Pharmakol.*, vol. 39, p. 1 (1897); Hoppe-Seyler, *Zeit. physiol. Chem.*, vol. 13, p. 66 (1889); Samuely, *Beitr. chem. Physiol. und Path.*, vol. 2, p. 355 (1902).

[2] Sostegni, *Landw. Vers.-Stat.*, vol. 32, p. 9 (1885); André, *Bull. Soc. Chim.* [3], vol. 21, p. 497 (1899); Eggertz, *Chem. Centralbl.*, 1889, p. 343.

[3] Scheibler u. Mittelmeier, *Ber. d. chem. Ges.*, vol. 22, pp. 1682 and 3118.

[4] Pasteur, *Ann. Chim. Phys.* [3], vol. 2, p. 257 (1842); Buchner u. Meisenheimer, *Ann.* (Liebig), vol. 349, p. 124 (1906); Henneberg, *Oest.-Ung. Zeitschr. Zuckerind. u. Landw.*, vol. 30, p. 1065 (1901).

[5] Fitz, *Ber. d. chem. Ges.*, vol. 17, p. 1188 (1884); Grillone, *Ann.* (Liebig), vol. 165, p. 127 (1872); Winogradsky, *Chem. Centralbl.*, 1902, ii, p. 709.

[6] Pasteur, *Ann. Chim. Phys.* [3], vol. 58, p. 323 (1860); Dubrunfaut, *Compt. rend. Acad. Sc.*, vol. 42, p. 945 (1856); Jodblauer, *Zeitschr. Verein. d. Zuckerind.*, vol. 38, p. 344 (1888); Schunk, *Ann.* (Liebig), vol. 66, p. 174 (1847).

So far as proteins are concerned, it was first thought that they have a constant composition and definite constant [7] properties. The modern researches revealed the fact that the various proteins have different chemical composition and structure, and accordingly they show different physical, chemical and physiological properties.

While the number of amino [8] acids out of which the protein molecule is chiefly built up is limited, the number of possible proteins is by far greater, for the reason that proteins can differ from each other either because they contain different amino acids or varying amounts of them, or because the amino acids can in the protein molecule follow each other in a different order, or may be linked with one another in a different way. Whatever the composition and structure of the proteins is, their gradual decomposition leads (through the stages of albumoses, propeptones, peptones) to diamino and monoamino acids. And it is just the latter compounds which play a rôle in the formation of humin substances.

A number of investigators [9] have found that proteins, when treated with acids, yield humus-like bodies. A further study of the phenomenon involved showed that it is particularly the diamino acid lysine [10] and the monoamino acids tryptophane [11] and tyrosine (and glucoseamine) that participate in the production of the melanoidins.[12]

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[7] A. Kossel, *Ber. d. chem. Ges.*, vol. 34, p. 3245 (1901).

[8] The discovery of leucine in cheese by Proust in 1818, and of tyrosine by Liebig in 1846, followed by discoveries of other amino acids, the number of which was more recently increased, thanks to the researches of E. Fischer and his school. A complete enumeration of them (including some synthetic amino acids) is given in Fischer's "Untersuchungen über Aminosauren. Polypeptide und Proteine," Berlin, 1906, pp. 19–23. See, also, E. Abderhalden and A. Weil, *Zeit. physiol. Chem.*, vol. 81, p. 207 (1912).

[9] Mulder, *Journal für practische Chemie*, vol. 21, p. 343 (1840); "The Chemistry of Vegetable and Animal Physiology," translated by D. P. H. Fromberg, Edinburgh and London, 1849, p. 153; O. Schmiedeberg, *Archiv. exper. Pathol. u. Pharmakol.*, 39 (1897); Panzer, *Zeit. physiol. Chem.*, vol. 33, p. 131 (1901).

[10] *Zeit. physiol. Chem.*, vol. 33, p. 355 (1901).

[11] Hopkins and Cole, *Jour. Physiol.*, vol. 27, p. 418 (1901), vol. 29, p. 451 (1903).

[12] F. Samuely, "Ueber die aus Eiweiss hervogehenden Melanine," Hofmeister's Beiträge, vol. 2, p. 355 (1902).

In connection with lysine, Hart [13] made the interesting observation in Kossel's laboratory that when proteins are hydrolyzed with acid in the presence of salts, *e.g.*, sodium chloride, they yield less humin substance and more lysine and ammonia; but when they are hydrolyzed with acid alone, they yield more humin substance and less lysine and ammonia.

While the humification in the soil of carbohydrates and proteins contained in plants, because of secondary influences, may in some measure represent a more complicated process than is the formation of melanoidins out of those substances when they are treated in the laboratory with acids or alkalies, yet it seems safe to state that plants containing proteins rich in tyrosine, tryptophane, lysine and glucoseamine will *ceteris paribus* yield more humus than plants poor in these compounds. On the other hand, protein-holding vegetable matter with a definite percentage of the amino acids mentioned may, on humification, yield varying amounts of humin substances, depending upon the conditions prevailing in the soil.

Inasmuch as carbohydrates and proteins form the bulk of vegetable and animal matter out of which humus-like substances are generally produced in the soil, it is now, in the light of our present knowledge, easy to grasp why humus has quite a complex chemical nature, just as the various carbohydrates, proteins, and their degradation products possess it in a greater or lesser degree.

However, the early investigators into the nature of humus, such as Berzelius,[14] Detmer,[15] Braconnot,[16] Malaguti,[17] Terreil,[18] and especially Mulder,[19] with a considerable number of workers who followed him, maintained that humus consists of but a few simple organic bodies which are chiefly acid in their nature (or at least can be converted into acids by treatment with alkalies), and which are closely related to each other. According to Mulder, *e.g.*, the ulmic acid, the first stage in decomposition of organic matter, is gradually converted into humic acid, geic acid,

[13] " Ueber die quantitative Bestimmung der Spaltungsproducte von Eiweisskörpern," *Zeit. physiol. Chem.*, vol. 33, p. 347 (1901).

[14] *Loc. cit.*

[15] *Landw. Versuchsstationen*, vol. 14 (1871).

[16] *Ann. Chim. Phys.*, vol. 12, p. 191 (1819).

[17] *Ann. Chim. Phys.* [3], vol. 54, p. 407 (1858).

[18] *Bulletin de la Soc. chim.* [2], vol. 44, p. 2 (1885).

[19] *Loc. cit.*

apocrenic and crenic acid, in the order named, all of which consist of but three elements, namely, of carbon, hydrogen, and oxygen. This conception of Mulder and contemporary writers may in part have been due to the fact that protein was at that time considered as being of constant definite composition, that the number of carbohydrates and of their disintegration products known was comparatively limited (which was also true of the protein products), and, last but not least, that the methods of research in the organic and biological chemistry were inadequate.

Since, as practice has shown, humus is of such vital importance to plant life that soils are in some measure valued according to their humus [20] content, it may not be out of place once more briefly to discuss the possible nature of the bodies resulting through decay of organic materials in the soil.

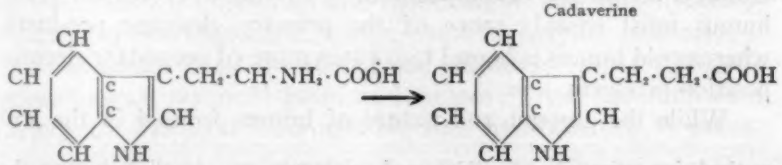
When pure proteins are subjected to the influence of enzymes or to the activity of micro-organisms, they are first hydrolyzed chiefly to diamino acids and monoamino acids. The resulting primary amino acids are, especially under the influence of microbes, subjected to secondary changes which lead to the formation of humin substances, of fatty and hydroxy acids, of phenols, basic substances, etc. Thus, the splitting off of CO_2 from the diamino acids as well as of the NH_2 group from the monoamino acids leads to the formation of amines and acids respectively, as illustrated by the following equations:

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH \cdot NH_2 \cdot COOH \longrightarrow CO_2 +$$

Lysine

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$$

Cadaverine



Tryptophane — Indolpropionic acid

[20] I wish to call attention to the great usefulness of the shaking machine which, upon recommendation of the writer, was introduced in the Michigan and Iowa Agricultural Experimental Stations. The shaker, which deserves to be used more generally in experiment stations, colleges, and elsewhere, can successfully and advantageously be applied practically in all cases where hand-shaking is required. The shaker is an excellent apparatus for preparation of extracts of all kinds, especially of humus extracts, for dissolving various substances, for ammonia determinations according to Schlösing's

In the case of nucleoproteids there result, in addition to protein products, purine derivatives and pyrimidine bases.

Equally when carbohydrates are subjected to the influence of enzymes and bacteria, they are, as the result of primary hydrolysis, first split into smaller molecules, still representing carbohydrates, which latter are then further decomposed, through fermentation, to alcohol, organic acids, etc.

In a similar manner the fats are split, under the influence of the agencies mentioned, into fatty acids and glycerol.

There is no reason to assume that the proteins, nucleoproteids, carbohydrates, and fats contained in the remains of vegetable and animal life, when subjected in the soil to the action of similar agencies, should not give the same decomposition products which result in the case of pure proteins, nucleoproteids, carbohydrates, and fats.

Now, broadly speaking, humus is bound to contain qualitatively the same constituents or, rather, elements as the remains of vegetable and animal life out of which it was formed. It is, however, plausible that the quantitative composition of humus which constantly undergoes changes in the soil will be different from what it was in the organic materials, for a number of reasons. In the first place, the comparatively easily soluble cleavage products are leached out of the soil organic matter, while the less soluble compounds accumulate in the humus. Equally, the chemically more resistant primary cleavage products will accumulate in the humus, while the less resistant bodies will undergo secondary decomposition. For this very reason fresh humus must contain more of the primary cleavage products, whereas old humus is bound to contain more of secondary decomposition products.

While the amount and nature of humus formed in the soil

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method, for estimation of solubility of substances, etc. In all such cases the employment of the shaker means saving of time, labor, and attention, at the same time affording a means for obtaining uniform results. There are a variety of shaking machines on the market. I have used with satisfaction the electrically-driven shaker as shown on page 418 of the Scientific Materials Company's catalogue for 1912, or on page 333 (No. 4589) of the catalogue of Eimer & Amend for 1905.

For instance, the extraction of humus from soils, which, according to the method of the Assoc. Off. Agr. Chem., requires 24 hours, can be accomplished in the shaker within some three hours.

primarily depends upon the quantity and character of the organic materials which undergo humification, it should be borne in mind that also other factors, like temperature, moisture, aëration of the soil, presence of certain chemical substances (salts, acids, etc.), as well as character and quantity of microbes contained in the soil, have more or less influence upon the nature of humus produced.

Whereas, with the full access of air and with suitable temperature and moisture conditions the process of eremacausis leads to a complete oxidation of the elements contained in humus materials whereby carbon is oxidized to carbon dioxide, hydrogen to water, nitrogen to nitric acid (through the stage of ammonia) and sulphur to sulphuric acid, the process of putrefaction leads to a number of intermediary products.

It happens comparatively seldom that in nature humification of organic materials takes place by one of the above processes to the exclusion of the other. More frequently both eremacausis and putrefaction set in, and while a part of the humus is entirely oxidized, the rest of it is decomposed to products a number of which have in the last few years been extracted from soils and identified as to their chemical nature. The results of this latter work show that humus—using this word in its widest sense—is of a very complex nature, consisting, as it does, of a large number of compounds. Contrary to the findings of earlier writers (see p. 568), humus contains, in addition to carbon, hydrogen, and oxygen, also nitrogen, sulphur, and phosphorus; it contains acids of well-known composition and constitution, like monohydroxystearic,[21] dihydroxystearic, oxalic, succinic, acrylic, saccharic; it contains bodies basic in nature, like diamino[22] acids (Kossel's hexon bases), purine[23] bases and amines;[24] it is made up of a variety of "neutral" compounds like hydrocarbons,[25] esters,

[21] Schreiner and Shorey, Bul. Nos. 53 and 74, Bureau of Soils, U. S. Dept. Agr.; *Journal Amer. Chem. Soc.*, 32, 1674 (1910); Original Communications, Eighth Intern. Congress Appl. Chem., vol. xv, p. 247.

[22] Jodidi, S. L., Tech. Bul. No. 4 (1909), Mich. Agr. Expt. Station; Research Bul. No. 1, Iowa Agr. Expt. Sta.; Jodidi and Wells, Research Bul. No. 3, Iowa Agr. Expt. Sta.

[23] *Loc. cit.*

[24] *Loc. cit.*

[25] Shorey, E. C., Original Commun., Eighth Intern. Congress Appl. Chem., vol. 15, p. 248 (1912).

aldehydes, as well as of bodies amphoteric in their nature, like amino [26] acids, etc.[27] Moreover, there can be very little doubt but that the number of definite organic compounds which can be extracted from soil organic matter will considerably be increased within the next few years. It is, however, a matter of course that humus of any one soil will contain only a part of the constituents enumerated above or yet to be found, and will in various soils differ in its composition, just as the various proteins, carbohydrates, and fats occurring in decaying organic materials show differences in their composition and constitution.

It may not be amiss to mention here that of the compounds found in soil organic matter the amino acids and acid amides play a prominent rôle because of the fact that they are contained in predominant proportions in acid extracts of soils, and for the further reason that they represent an important source for the production in the soil of ammonia,[28] and hence of nitrates.

Taking into consideration that certain constituents—the ten well-known elements—are absolutely indispensable for plant life, it is easy to understand why humus is called by many the life of the soil. Not only does it contain most of the elements which were recognized to be necessary for plant life, like nitrogen, phosphorus, sulphur, etc., but, what is of equally great importance, it affords a means for rendering more of the necessary inorganic elements available. The carbon dioxide, which is gradually being formed through oxidation of a part of the humus carbon, represents in combination with water a powerful agent for dissolving rocks and making the elements potassium, magnesium, calcium, and others contained in them available. Equally, as is known, the nitric acid and sulphuric acid, which result through oxidation of the elements nitrogen and sulphur present in humus, are strong agents for dissolving the indispensable elements out of the rocks,

[26] Jodidi, S. L., *Journal Amer. Chem. Soc.*, vol. 32, p. 396 (1910), vol. 33, p. 1226 (1911), vol. 34, p. 94 (1912); Schreiner, O., and Shorey, E. C., *Journal Biol. Chem.*, vol. 8, p. 381 (1910); Robinson, C. S., Tech. Bul. No. 7, Mich. Agr. Expt. Sta.; *Journal Amer. Chem. Soc.*, vol. 33, p. 564 (1911).

[27] A good account of the compounds extracted from soils is contained in Original Commun., Eighth Intern. Congress Appl. Chem., vol. 15, pp. 248–250.

[28] Jodidi, Kellogg and Snyder, Research Bul. No. 9, Iowa Agr. Expt. Station; Jodidi, JOURNAL OF THE FRANKLIN INSTITUTE, vol. 175, p. 245 (March, 1913); *Ibid.*, p. 483 (May, 1913); Original Communications, Eighth Intern. Congress Appl. Chem., vol. 26, p. 119 (1912).

that way converting rocks and rocky land into fertile, arable soil.

It is also well known that humus improves the physical condition of the soil. It increases, for instance, its capacity to hold water, to retain valuable nitrogenous constituents, to resist corrosion; it binds the particles of sandy soils; it makes clayey soils friable, increasing at the same time the capacity of the soil to absorb the sun's rays and making the soil temperature more uniform. In other words, humus makes the soil a more habitable and suitable home for the performance of the life functions of plants.

Thus we find the humification process inserted into the chain of Nature's cycles as a most necessary link, without which the perpetual continuance of plant life cannot very well be conceived. Again, man's food, whether of vegetable or animal origin, is composed chiefly of proteins, fats, carbohydrates, and some mineral substances, all of which are contained in the plant and animal body. Animal life, however, is, in the last analysis, based upon the presence of plants, the digestion and assimilation of which gives the material for the formation in the animal body of its organs and tissues. Again, the plants need for their life certain elements which are present in humus. Here we have, then, a cycle in which physical life of man, as well as the existence of the animal and vegetable kingdoms, is brought into close connection with humus. So close is this relation that conditions indispensable for life are also necessary for decomposition of humus materials, and that extremes excluding life render also decomposition impossible. There is practically no plant life in Arctic regions or throughout the winter, and there is no decomposition under the same conditions. On the other hand, plant life is luxurious in the tropics. There, too, decay is very rapid. The plant and animal kingdoms need for their life air. The same air is indispensable for decomposition. Equally, neither plant life nor decomposition of organic substances is possible without water. The above coherence means that in the process of humification Nature has a powerful means for the utilization of vast amounts of waste materials for purposes of life.

Office of Physiological and Fermentation Investigations,
Bureau of Plant Industry,
U. S. Department of Agriculture.

Safety of Life at Sea.—Recommendations of the committee appointed by the Secretary of Commerce for the use of the American delegation to the International Conference on Safety of Life at Sea to be held in London during the present month:

1. That efficient apparatus for the radio communication be required on all ships in foreign trade which carry 50 persons or more (passengers or crew, or both combined), navigating the ocean between ports more than 200 nautical miles distant from one another.

2. That apparatus, to be deemed efficient, must transmit messages with sufficient power to be received by day over sea at a distance of at least 100 nautical miles by a ship equipped with apparatus equal to that of the transmitting ship.

3. That an auxiliary power supply should be provided, independent of the vessel's main electric power plant, which will enable the sending set for at least four hours to send messages over a distance of at least 100 nautical miles by day.

4. That (*a*) two first-grade operators should be required on all such ships maintaining a constant service, also on all such ships carrying 100 or more passengers.

(*b*) One first-grade and another first- or second-grade operator should be required on all other such passenger ships.

(*c*) One operator (first or second grade) and one cargo operator or watcher should be required on all such cargo boats.

The recommendations of the committee are based not only on the laws of the United States but also in principle on the London International Convention and the laws of Canada and Australia. The laws of Canada and Australia do not specifically require a constant wireless watch on cargo boats, but authorize the administrations of those colonies to impose that requirement.

The second operator or watcher on a cargo boat will rarely be required for the safety of his ship or the crew of which he is a member. The constant watch is to be maintained almost entirely for the purpose of enabling the master of the cargo boat to be at all times in a position to receive radio distress calls and to render the assistance within his power. The proposition, accordingly, is in the interests of the safety of the seafaring world, and is, in effect, a tax upon the owners of such cargo boats for the promotion of the safety of others.

The committee comprised E. T. Chamberlain, Commissioner of Navigation, Chairman; W. H. G. Bullard, Captain, U. S. Navy, Superintendent Naval Radio Service; C. McK. Saltzman, Major, U. S. Army, Assistant to Chief Signal Officer; Jno. Q. Walton, Constructor, Revenue-Cutter Service; Frederick A. Kolster, Bureau of Standards.

Silver Solder. ANON. (*Brass World*, ix, 9, 306.)—Silver solder is far superior to spelter solder for brazing metals, as it melts more readily and forms a stronger and tougher joint. As its advantages are appreciated it is becoming more and more extensively used.

A NEW AUTOMATIC FIRE ALARM.*

BY

F. A. J. FITZGERALD,

FitzGerald and Bennie Laboratories, Niagara Falls, N. Y.
Member of the Institute.

So MUCH has been published in recent years in regard to the enormous annual loss from fires that nearly every one knows the magnitude of the problem and the importance of adequate fire protection. One result has been the extension of the use of sprinkler systems, and it is unquestionable that these have greatly reduced the fire losses. However, for obvious reasons there are many places where the installation of sprinkler systems is not feasible and where, nevertheless, the use of some form of fire protection is desirable. Moreover, even where the sprinkler system is in use it is important that an alarm of fire should also be given, and if this can be made automatic—so much the better.

For more than a year a very ingenious device for use as an automatic fire alarm has been the subject of considerable research work in this laboratory, and it is believed that a detailed description of it and its method of manufacture will be of interest.

GENERAL PRINCIPLE.

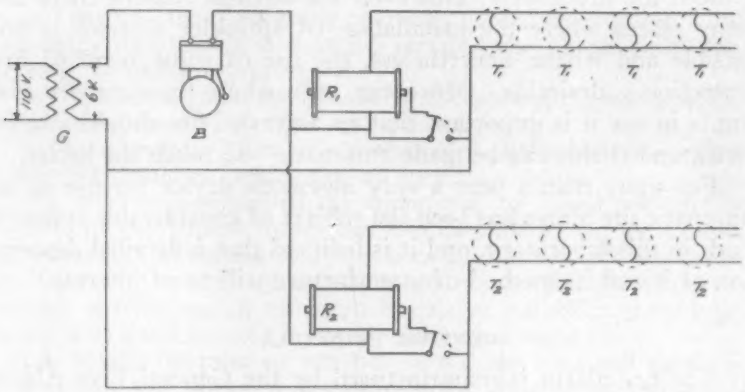
The fire alarm is manufactured by the General Fire Alarm Corporation, and is the invention of Mr. Eugene Garretson. It consists in the use of a thermoscope in which the active element is a substance having a negative temperature coefficient of electrical resistance. The thermoscope forms part of an electric circuit, which also contains an alarm gong and indicating device, but has such a high resistance under normal conditions that the current passing through the circuit is not sufficient to work the alarm. If, however, the temperature of the air surrounding the thermoscope rises to a certain degree the electrical resistance drops so as to permit the passage of sufficient current to give the alarm.

In Fig. 1 is shown the wiring diagram of a fire detector for two stations. The source of the current for the circuit is shown

* Communicated by the author.

at G, the alarm gong at B, and relays with drops at R_1 and R_2, corresponding to the two stations protected with the series of thermoscopes T_1 and T_2 respectively. If the circuits are traced it is seen that they are complete only through the normally high resistance thermoscopes, and consequently the current is not sufficient to trip the relays nor to release the mechanical gong. Suppose, however, that a fire occurs in the room where the thermoscopes T_1 are installed, the resistance of one or more of these will be sufficiently lowered to permit the passage of current that will trip the relay R_1, thus indicating where the fire is and closing absolutely the alarm gong circuit.

FIG. 1.



Fire alarm circuit.

THE THERMOSCOPE.

So far as the general principle of the invention is concerned, it is plain that a large number of substances might be used as the sensitive element of the thermoscope,—in fact, any substance with a negative temperature coefficient; but for practical purposes the substance should have other qualities than the mere possession of a negative temperature coefficient.

A thermoscope of this kind should have the following characteristics:

(1) A very high resistance at ordinary temperatures.

(2) A large temperature coefficient, so that a small increase in temperature produces a large decrease in resistance.

(3) Its heat capacity should be small, so that as the resistance drops the increase in current, even though a very small one, passing through the thermoscope tends to heat it, and thus greatly increases the sensitiveness of the detector as the critical temperature is approached.

(4) Its characteristics should be permanent under all conditions to which it is apt to be exposed.

One of the best of the substances which have been found for this purpose, and to which Mr. Garretson applies the general name *thermitite,* is a preparation of silver sulphide.

ELECTRICAL PROPERTIES OF THERMITITE.

Before considering the properties of *thermitite* as investigated in this laboratory it will be well to describe the thermo-

FIG. 2.

Thermoscope.

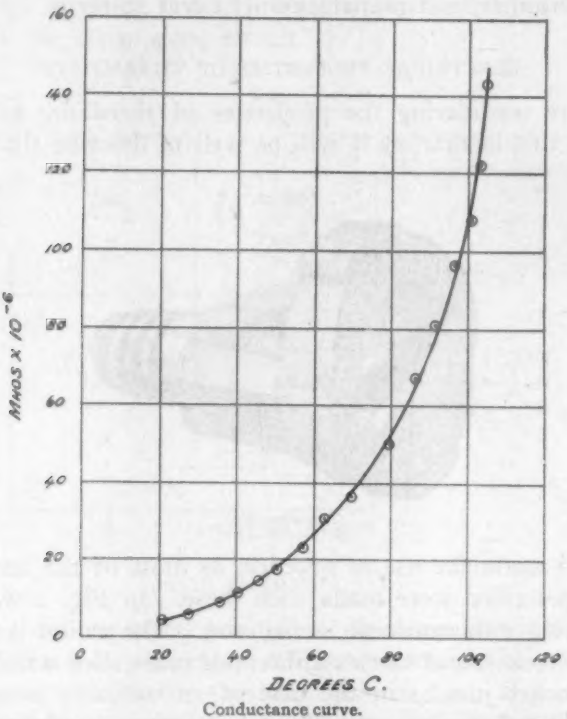
scopes as made for use in practice, as most of the tests which will be described were made with these. In Fig. 2 we have a cut showing a thermoscope, actual size. The mount is made of glazed porcelain and carries a threaded brass shell which screws into a socket just as in the case of an ordinary incandescent lamp. The *thermitite* strip has copper wires fused to its ends, and these are soldered to the contacts.

If one of these thermoscopes is put in a circuit with a small six-volt tungsten lamp and three dry cells connected in series the lamp will not light up; but if a lighted match is held under the *thermitite* the lamp almost instantly begins to glow with full candle-power. If the match is removed and the piece of *thermitite* cooled in any way the lamp is extinguished.

This, however, would not be the method when using the *thermitite* for a fire alarm, since that substance is an electrolyte, and, even though a solid, electrolytic changes might be expected were a direct current used in the circuit. That electrolysis does occur may be shown by the following experiment:

A piece of *thermitite* provided with silver electrodes was placed in a direct-current circuit for some time. Then the *thermitite* was cut out of the circuit and the electrodes connected to the terminals of a sensitive galvanometer which was immediately deflected, showing the generation of a current in the opposite direction to that which had been passed through in the direct-current circuit.

FIG. 3.



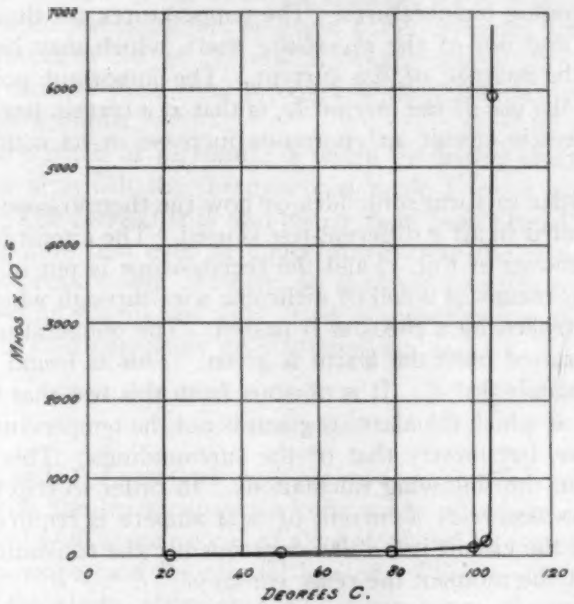
Conductance curve.

The experiment clearly shows a phenomenon-like polarization in an ordinary electrolytic cell. Obviously, then, in the use of

thermitite as a thermoscope an alternating current must be used. It also indicates the necessity of using an alternating current in any attempt at making measurements of the electrical resistance of the thermoscope. The study of the behavior of silver sulphide as an electrolyte must be reserved for a future paper, as the work on it is not yet complete, for it was necessary first to develop a commercial thermoscope rather than make a complete investigation of the electrical properties of the thermitite.

An investigation of the change of resistance of *thermitite*

FIG. 4.



Conductance curve.

with temperature has been made with the express object of studying its action when used as a thermoscope. For this purpose a bridge was used, the current being supplied by a small induction coil and a high-resistance telephone receiver taking the place of a galvanometer. The thermoscope was immersed in an oil-bath heated by a coil of wire through which a current was passed. A rheostat was used to regulate the current so that the temperature of the oil-bath, which was kept thoroughly stirred,

could be controlled. The result of one of these experiments is given in the curves of Fig. 3 and Fig. 4, where the abscissæ are degrees Centigrade and the ordinates are mhos $\times 10^{-6}$.

Referring to Fig. 3, the curve shows the increase in conductance from 4.3×10^{-6} mhos at 21° to 143×10^{-6} mhos at 104°. Then a very abrupt change was observed, for at 105.5° the conductance was 5880×10^{-6} mhos. This sudden change is shown best in the curve of Fig. 4, which is from the same observations, but plotted on a different scale.

Now it is not pretended that the curves shown in Fig. 3 and Fig. 4 represent the true conductance of the thermoscope at the corresponding temperatures. The temperatures are those of the oil-bath and not of the *thermitite* itself, which may be higher, due to the passage of the current. The important point, considering the use of the *thermitite*, is that at a certain temperature in an electric circuit an enormous increase in its conductivity occurs.

In order to form some idea of how the thermoscope behaves when heated in air a different test is used. The circuit is similar to that shown in Fig. 1, and the thermoscope is put in an oven heated by means of a coil of nichrome wire through which a current controlled by a rheostat is passed. The temperature of the oven is raised until the alarm is given. This is found to be at approximately 80° C. It is obvious from this test that the temperature at which the alarm is given is not the temperature of the *thermitite*, but merely that of the surroundings. This may be seen from the following calculations. In order to trip the drop of the 80-ohm relay a current of 0.04 ampère is required. The e.m.f. of the circuit is 6 volts, consequently the resistance of the circuit at the moment the relay works is

$$\frac{6}{0.04} = 150 \text{ ohms},$$

but the resistance of the relay is 80 ohms, consequently that of the thermoscope is only 70 ohms. The oil-bath test showed that at 80° the resistance of the thermoscope was 19,000 ohms, so it is plain that its temperature when the alarm is given is very much higher than that of the surrounding air. This, of course, is due to the heating effect of the current. Here we have an explanation of the great sensitiveness of the thermoscope, for it

does not simply depend upon the heating effect of the air to cause it to give the alarm. Indeed, it would be more accurate to say that the thermoscope fails to give an alarm because of the cooling effect of the surrounding air, and that when this cooling effect is removed the thermoscope becomes a good conductor and turns in an alarm.

MANUFACTURE AND TESTING.

The process of manufacturing the thermoscopes is simple. The *thermitite* is made in sheets 0.5 mm. thick, and from these oval-shaped pieces 10 mm. long and 5 mm. wide are punched out. Short pieces of No. 26 (B. and S. gauge) copper wire are fused to the ends of these oval pieces, and they are then put in the porcelain mounts.

Every batch of *thermitite* is tested by finding the oven temperature at which the thermoscopes made from it ring in the alarm. The *thermitite* is also tested in an oven heated to 65° C. to make sure that even at temperatures near the critical one it will not break down. Finally, all thermoscopes are mounted in large testing boards and kept under observation for at least one month to discover if any defects develop.

FIRE TEST.

The tests for practical work are made as follows: In a room fitted with the thermoscopes a cone made of asbestos board is moistened with about 50 c.c. of alcohol, placed on the floor under a thermoscope, and the alcohol ignited. This is quite sufficient to give the alarm, although a dial thermometer mounted beside the thermoscope fails to show more than a rise of 5 degrees C. in the temperature, nor after repeated tests has the slightest effect been observed on the varnish with which the wooden ceiling of the room is coated. No doubt, if the asbestos cone was not placed directly under the thermoscope it would be necessary to use a larger quantity of alcohol, but the test as performed shows that before the hot air about the thermoscope can even scorch varnish or cause a dial thermometer to register more than a few degrees rise in temperature the alarm is given.

PERMANENT CHARACTER.

In order to find out if the thermoscopes were permanent, some were mounted out of doors, where they would be exposed to all conditions of weather, with entirely satisfactory results. To test resistance to the action of chemicals several thermoscopes were mounted on the ceiling of our chemical laboratory where they are exposed to the acid fumes, etc., characteristic of such a room, and no deterioration has been observed.

CONCLUSION.

As a result of the study of the thermoscopes it appears that for use as a fire alarm they are highly satisfactory for several reasons. They are extremely sensitive, because the immediate cause of the heating of the *thermitite* is the electric current of the circuit, and this is prevented simply by the cooling effect of the surroundings under normal conditions. Any heating of the surroundings not only raises the temperature of the *thermitite* by the heat which these give off, but at the same time increases the flow of current and consequently increases the heating effect. When the resistance is diminished one-half the current is doubled, and, since the heating effect is proportional to the product of the square of the current and the resistance, the heating effect is doubled. In fact, the system might be described as being always in a state of unstable equilibrium.

The construction of the whole system is extremely simple, being practically equivalent to an ordinary electric bell equipment with the thermoscopes replacing the push-buttons. The thermoscopes themselves are so simple in construction that they can be treated much as are incandescent lamps. Thus, enclosed in a suitable cage they may be attached to extension cords and put in places otherwise difficult to protect, such as in the cargo stowed in the holds of ships.

The tests of the *thermitite* show its permanent character. Outside of mechanical breakage the only possibility of failure is in the direction of a lowering of the electrical resistance, which would automatically indicate that there was trouble at that point.

Finally, before closing it may be of interest to note that a new use of the thermoscope as a detector of hot bearings is at present the subject of further research.

THE TWELFTH INTERNATIONAL GEOLOGICAL CONGRESS

BY

R. A. F. PENROSE, JR.*

THE meeting of the Twelfth International Geological Congress was held in Toronto, Canada, August 7–14, 1913. Before and after the meeting numerous geological excursions were taken by the members of the Congress in various parts of Canada, while during the meeting short excursions were taken in the vicinity of Toronto. The excursions before and after the meeting, however, were often of considerable length, the different trips covering most of Eastern Canada and extending through Western Canada as far as the Pacific Coast and the Yukon Territory. Some of the excursions began before the middle of July and others lasted until after the middle of September, so that, though the actual meeting at Toronto lasted but seven days, the movements of the Congress lasted over two months. There were in all over thirty different excursions.

The various excursions were under the guidance of Canadian geologists familiar with the regions traversed. They were excellently conceived and carried out, every provision was made for the comfort of the members, and the opportunity to see a great deal of geology in a short time and under most advantageous conditions was remarkable. Special guide-books for many of the excursions were published by the Canadian geologists and were remarkably comprehensive in their scope; in fact, they were textbooks of the geology of the regions traversed. The excursions were so arranged that the geologists coming from Europe and other places to the East could see Eastern Canada before coming to Toronto, and, after attending the general meeting at Toronto, could proceed westward on the excursions in that direction.

The proceedings of the Congress at Toronto were full of interest to all who attended them. The honorary president of the Congress was the Governor-General of Canada, the Duke of Connaught; the president was Prof. Frank D. Adams, of McGill

* Mr. Penrose and Mr. E. V. D'Invilliers were official delegates of the Institute.

University, Montreal; the general secretary was R. W. Brock, Director of the Geological Survey of Canada; and the secretary was W. Stanley Lecky. The meeting was opened with speeches of welcome by the Right Honorable Sir Charles Fitzpatrick, Chief Justice of the Supreme Court of Canada; the Honorable W. H. Hearst, Minister of Lands, Forests and Mines; Acting Mayor Church, of Toronto, and President Falconer, for the University of Toronto.

The committees appointed to study various subjects presented their reports, while general discussions on many important topics were carried on at special meetings, and informal discussions were numerous. The committee reports presented were from:

1. International Glacier Committee.
2. Committee of the International Geological Map of Europe.
3. Palæontologia Universalis Committee.
4. Spendiarow Prize Committee.
5. Stratigraphical Lexicon Committee.
6. Committee on Valuation of Iron Ore Resources.
7. Committee on Institute for Study of Volcanoes.
8. Fossil Man Committee.

The principal topics for general discussion were:

1. Coal Resources of the World.
2. Differentiation in Igneous Magmas.
3. The Influence of Depth on the Character of Metalliferous Deposits.
4. The Origin and Extent of the pre-Cambrian Sedimentaries.
5. The Subdivisions, Correlation, and Terminology of the pre-Cambrian.
6. To what Extent was the Ice Age Broken by Interglacial Periods?
7. The Physical and Faunal Characteristics of the Palæozoic Seas with Reference to the Value of the Recurrence of Seas in Establishing Geological Systems.

In addition to the above subjects numerous other topics were introduced and considered during the meeting.

The most elaborately treated subject was the "Coal Resources of the World," on which a monograph had been pre-

pared under the direction of the Canadian members of the Congress. It comprises three quarto volumes and an atlas, and the different parts of it are written by geologists of different countries. The coal resources of over sixty countries are described, most of the papers being in English and all being summarized in English. The publication, in fact, is a compilation of papers on the coal of every section of the world, written by specialists on each field. It is a wonderful work and reflects credit alike on the individual writers and on the Canadian geologists who compiled and edited it. At the last previous meeting of the Geological Congress, which was in Stockholm in 1910, a similar monograph on the "Iron Ore Resources of the World" was gotten up for the occasion and the precedent has now been strongly set for similar monographs on important geological subjects to commemorate future meetings.

The International Geological Congress as an organization is over thirty-five years old and had its origin at the Centennial Exhibition in Philadelphia in 1876, where a collection of maps and other geological records of different parts of the world called the attention of scientists to the desirability of international meetings to facilitate the exchange of ideas and data among the geologists of the world. At a meeting of the American Association for the Advancement of Science in Buffalo, in the summer of the same year, the idea was further elaborated, and a commission was appointed to organize an international geological congress to be held in Paris at the time of the exhibition there in 1878. The plan was carried out, and over twenty different countries were represented by delegates at this first Congress. So successful was it that the Congresses have been held at intervals of about three years ever since and the meetings have taken place in different parts of Europe and America. Over twenty years ago the Congress met in Washington; this year it was held in Canada, at the invitation of the Canadian Government, and the next Congress will be held in Belgium, at the invitation of that country.

The International Geological Congress is governed by a council, but usually the country in which the Congress meets makes what general arrangements it sees fit for conducting the proceedings. At the Toronto meeting, however, steps were taken to formulate an arrangement for a permanent organization to direct the methods and procedures of the meetings wherever held.

About nine hundred members were enrolled in the lists of the Twelfth International Geological Congress, and of this number about four hundred and fifty were actually present. The Canadians and Americans were the most numerous, though there were also many members from Great Britain and Germany, while France, Italy, Russia, Austria, Belgium, and Sweden sent large delegations, and Norway, Argentine Republic, Japan, China, and many other countries were well represented; in fact, delegates from over forty different countries were present, so that the Congress was international in fact as well as in name. The various governments, as well as many of the great universities and scientific societies throughout the world, were represented by delegates.

The management of the Congress by the Canadians was excellent. Everything was done that could add to the comfort, interest, and pleasure of the members. The people of Toronto and of Canada in general were most hospitable and kind, and no member of the Congress could have left Canada without the pleasantest recollections of its people and their boundless hospitality.

New Central Battery Telephone Traffic Distributer. V. J. BAUMANN. (*Elektrotechn. Zeitschr.*, xxxiv, 583.)—In central battery manual telephone exchanges each subscriber has individual calling and cut-off relays with signal lamps. The subscribers are divided into groups, each of which is assigned to an answering or A operator. The calling rate differs not only at various times of the day, but also for different subscribers, and the work thrown on the operators is consequently very unequal. Avén, of Stockholm, has modified the usual arrangement by automatically indicating to the A operator a disengaged B operator, and the adoption of this modification has resulted in a reduction in the size of the multiple by about 50 per cent. The more evenly the work can be distributed among the operating staff, the more efficiently can the apparatus be used and economies in equipment and operating can be effected. The author describes a central battery automatic traffic distributer, in which all incoming calls are equally distributed to the operating staff. The subscribers' equipment is reduced at the exchange, as there is no necessity for calling and cut-off relays or answering jacks, and consequently there are no relay racks required and the I. D. F. is dispensed with. The circuit arrangements are such that no operator receives more than one call at any given instant. The paper should be referred to for a full description of the arrangement with the accompanying diagram.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THE MELTING-POINTS OF SOME REFRACTORY OXIDES.†

By C. W. Kanolt,
Bureau of Standards.

THE oxides were melted in a graphite resistance furnace. The melting-points were determined by means of heating curves, the temperatures being measured with a Morse optical pyrometer of the Holborn-Kurlbaum type.

The pyrometer was calibrated against the melting-points of antimony (630°), copper-silver eutectic (779°), silver (960°), copper (1083°), and diopside (1391°). Absorption glasses were used in measuring temperatures above 1400°. As a check upon the work five determinations of the melting-point of platinum were made in an iridium furnace. The weighted mean was 1755°, with an average deviation of 5°. This is identical with the value accepted by the Bureau of Standards.

The greatest difficulties in work with the oxides are the avoidance of smoke, which would give low temperature readings, and the prevention of the contamination of the oxide by the material used as a support.

Magnesia was melted in graphite, alumina in graphite and in tungsten, chromium oxide in tungsten, and lime in tungsten. Lime was also made into tubes, which were supported by the upper end in the cooler part of the furnace, while the lower end extended into the hottest part and was melted. The pyrometer was sighted into the tube. When crucibles were used, slender tubes of the same material as the crucible were inserted in the material to be melted and the pyrometer was sighted down these tubes.

Smoke may be avoided by the use of a sufficiently high vacuum, but lime and magnesia could not be melted in a vacuum on account of rapid vaporization. In these cases the furnace was filled with hydrogen or other gas at atmospheric pressure, and the inner tube was kept free from smoke by a gentle current of the gas.

* Communicated by the Bureau.

† Shortly to appear as scientific paper reprint from the Bulletin of the Bureau of Standards.

The cooling effect of the gas current was found to be negligible. When a lime tube was used it was freed from smoke in the same way.

The method in which the material to be melted is made into a tube appears to be the most promising one for further use.

The results are summarized in the following table:

Oxide	Melting-point, Centigrade degrees.	Number of determinations.	Average deviations, degrees.
MgO	2800	6	13
CaO	2572	5	3
Al_2O_3	2050	8	4
Cr_2O_3	1990	5	6

THE PENTANE LAMP AS A WORKING STANDARD.*

By E. C. Crittenden and A. H. Taylor.

FOR several years an investigation of various flame standards of candle-power has been in progress at the Bureau of Standards. This investigation has been made with the double purpose of determining whether any of the flame lamps are capable of furnishing a check on a possible drift in the value of the unit now maintained by electric incandescent standards, and of finding a satisfactory working standard for use where electric standards are impracticable.

The results have been distinctly favorable to the use of the Harcourt 10-candle pentane lamp as a secondary standard. This lamp has the disadvantages of being large and not easily portable, of using fuel which is expensive and somewhat dangerous, and of requiring more air than ordinary ventilation will supply. In spite of these faults its use is increasing, chiefly because it appears to be the only standard of candle-power now in use, other than incandescent electric lamps, which can be relied upon to give, under the usual working conditions, the degree of accuracy expected in present commercial practice.

A given lamp will repeat its value very closely, but the normal candle-power is usually not exactly ten, and the exact value must be determined by a photometric test. Since the lamp itself is only an instrument for producing the actual standard, the flame, there is little significance in a value given for the lamp unless other

* To be published in the *Bulletin of the Bureau of Standards* and in the *Transactions of the Illuminating Engineering Society.*

factors, such as air and fuel and other conditions of operation, are known. The value certified for a lamp applies strictly only for its use under conditions identical with those under which it was standardized; a large part of the paper is therefore devoted to a description of the method of testing followed at the Bureau of Standards and to general directions for the use of the lamps.

Especial attention is given to the effects of variation in pentane and of atmospheric conditions. It is found that the pentane commercially obtainable increases in density rather rapidly by the fractional distillation which occurs in the lamp. The density (at 15° C.) should be between 0.6235 and 0.626, but it usually reaches 0.635 when a little over half of the liquid has been used. Beyond this point there is a marked increase in the intensity of the flame as the density of the fuel becomes greater. For an approximate correction, which will make possible a considerable economy in fuel without much sacrifice in accuracy, the variation may be assumed to be linear and to be one per cent. in candle-power for each 0.01 in the density of the liquid.

When the lamps are operated in a well-ventilated room the most important cause of variation is humidity. Water vapor in the air lowers the intensity of the flame, the decrease being proportional to the amount of vapor. Since variations due to this cause may exceed 15 per cent., the water vapor correction is very important. Previous work at the Bureau * has indicated that one per cent. of water vapor in the air causes a decrease of 5.67 per cent. in the candle-power of the pentane flame, whereas the correction officially established in England is 6.6 per cent. The present paper gives further data based on about 75,000 photometer settings on 27 lamps, including all those tested in 1911 and 1912, whose tests have extended over a range of 0.5 per cent. or more of water vapor in the air. The mean result is an exact check of the correction factor previously found at the Bureau.

To facilitate the reduction of observations on flames to normal candle-powers, a chart is given from which the departure of a lamp from normal value can be read directly when the barometric pressure and the readings of the wet and dry bulb thermometers of a ventilated hygrometer are known. The chart is plotted for the pentane lamp, but it may be applied to other flames without introducing serious errors. It would certainly be justifiable to measure

* Rosa and Crittenden, *Trans. Illuminating Engineering Society*, 5, p. 753 (1910).

gas flames, for instance, with electric standards and to correct the observed candle-powers to obtain normal values according to the chart.

PYROMETER TESTING AND HEAT MEASUREMENTS.*

THE object of this circular has been to answer as far as possible the frequent inquiries addressed to the Bureau concerning high temperature measurements, the general use of pyrometers, the regulations governing their acceptance for test, etc., and to briefly discuss various technical points which are of especial importance in this field of work. The following topics are treated:

1. Temperature scale.
2. Thermoelectric pyrometers.
   - (*a*) Homogeneity.
   - (*b*) Annealing.
   - (*c*) Precautions.
   - (*d*) Calibration.
   - (*e*) Temperature of cold junction.
   - (*f*) Use of a pyrometer galvanometer of low resistance.
   - (*g*) Temperature coefficient of galvanometer.
3. Electrical resistance thermometers.
   - (*a*) Calibration.
4. Optical and radiation pyrometers.
   - (*a*) Calibration.
5. Expansion and other pyrometers.
   - (*a*) Recording instruments.
6. Heat measurements.
7. Publications in thermometry, pyrometry, and heat measurements. (Bureau of Standards Bulletin.)
8. Regulations concerning tests.
   - (*a*) Application for test.
   - (*b*) Identification marks.
   - (*c*) Shipping directions.
   - (*d*) Address.
   - (*e*) Remittances.
   - (*f*) Breakage.
9. Fees.

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* Circular of the Bureau of Standards No. 7, 5th edition, October 1913, 16 pages.

THE FRANKLIN INSTITUTE

(Proceedings of the Special Meeting, held Thursday, October 2, 1913.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, October 2, 1913.

In pursuance to the following call:

THE FRANKLIN INSTITUTE,
15 South Seventh Street,

September 27, 1913.

A Special Meeting of the Institute will be held on Thursday, October 2d, at four o'clock P.M., in the Hall of the Institute, to determine whether the site acquired at Sixteenth and Arch Streets for the use of The Franklin Institute has become unsuitable for or unadapted to the purposes of The Franklin Institute, and to pass upon the action of the Board of Managers in acquiring a new site.

R. B. OWENS,
Secretary.

a special meeting of the Institute was held this afternoon at four o'clock.

PRESIDENT WALTON CLARK *in the Chair.*

A quorum being present, Mr. Henry Howson, Chairman of the Institute's Franklin Fund and Building Committee, stated that the Board of Managers recommended to the Institute the sale of the Institute's property on the southeast corner of Sixteenth and Arch Streets, it having become unsuitable and unadapted to the purposes of the Institute by reason of the plotting across its surface of the Park Boulevard, and offered the following resolutions, which were unanimously adopted:

"Resolved, That, in the judgment of the members of The Franklin Institute, the plot of ground situate on the southeast corner of Sixteenth and Arch Streets, 44 feet on Arch Street by 150 feet on Sixteenth Street, acquired for the purpose of erecting thereon a building for the use of The Franklin Institute, has, by reason of the plotting across its surface of the Park Boulevard, become unsuitable for and unadapted to the purposes of The Franklin Institute, in carrying out the provisions of the trust created under the agreement of February 4, 1907, with the City of Philadelphia, therein created Trustee.

"Resolved, That the City of Philadelphia, Trustee, is hereby requested and authorized to sell the said lot of ground situate on the southeast corner of Sixteenth and Arch Streets, 44 feet on Arch Street by 150 feet on Sixteenth Street, for such price and upon such terms as may to it seem right and proper, and that the purchaser under such sale shall take title, without

any responsibility concerning the application of the purchase money or other consideration; we hereby consenting to such sale, and to the application of the proceeds thereof in the purchase by the said City of Philadelphia, Trustee, of other premises and the erection thereon of another building or buildings for the purposes and upon the trusts prescribed in the said agreement of February 4, 1907.

"*Resolved,* That the proper officers be, and they are hereby, authorized to certify to the passage of the above resolution and to attach the seal of the Institute thereto.

"*Resolved,* That the President of The Franklin Institute be authorized, on behalf of said Institute, to join with the City of Philadelphia, Trustee, in a petition to the Court of Common Pleas of Philadelphia County, setting forth the fact that the plot of ground situate on the southeast corner of Sixteenth and Arch Streets, 44 feet on Arch Street by 150 feet on Sixteenth Street, acquired for the purpose of erecting thereon a building for the use of The Franklin Institute, has, by reason of the plotting across its surface of the Park Boulevard, become unsuitable for and unadapted to the purposes of The Franklin Institute, in carrying out the provisions of the trust created under the agreement of February 4, 1907, with the City of Philadelphia, therein created Trustee, and asking the consent of the said Court to the sale of said property for such a price and upon such terms as may be fixed by the City of Philadelphia, Trustee, and to the application of the proceeds thereof in the purchase by the said City of Philadelphia, Trustee, of other premises and the erection thereon of another building or buildings for the purposes and upon the trusts prescribed in the said agreement of February 4, 1907."

Mr. Howson then stated that the Board of Managers had obtained options on the following properties between Race and Cherry Streets: 1826, 1828, 1830, 1832, and 1834 Race Street; 133, 137, 139, and 141 North Nineteenth Street, and asked the Institute's approval of this choice by the Board of Managers of a site for a new building.

On motion, duly seconded, it was resolved that the action of the Board of Managers in securing options on the above properties be approved and that the Board of Managers be requested to complete the purchase.

R. B. OWENS,
Secretary.

(*Proceedings of the Stated Meeting held Wednesday, October 15, 1913.*)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, October 15, 1913.

VICE-PRESIDENT JAMES M. DODGE *in the Chair.*

Additions to membership since last report, 105.

The following proposed amendment to the By-laws, presented at the May meeting, was submitted for final action:

Article iv, Section 1, of the By-laws to be amended by striking out everything after "January" in the third line, and substituting the following words:

"March in each year shall pay, in advance, for the current year, one-half of the annual dues," so that the section as amended will read:

"The annual payment of fees for membership shall be due and payable on the first of October in each year, in advance; but all members elected after the 31st of March in each year, shall pay, in advance, for the current year, one-half of the annual dues."

On motion, duly seconded, the amendment was adopted.

The Chairman then introduced Mr. Emile Berliner, of Washington, D. C., who presented a communication on "The Revolving Cylinder Internal Combustion Motor."

Revolving cylinder motors present mechanical problems and mechanical movements differing from those of reciprocating motors and from turbines, and they are a class in themselves, taking a position between the two others. The mechanism is non-reciprocating, but the gas action is, and this fact enables them to give as much power as reciprocating motors, but with the smoothness of running of a turbine. Centrifugal force is the most important factor to be dealt with and furnishes problems of great difficulty. The subject was illustrated by working models and diagrams.

A discussion followed the reading of the paper, and the following gentlemen participated: Messrs. Henderson, Levy, Bilgram, Morris, Stratton, Crisfield; Professors Fernald and Barnes, and others.

On motion, duly seconded, the thanks of the meeting were extended to the speaker and the paper was referred for publication.

Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, October 1, 1913.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, PA., October 1, 1913.

DR. GEORGE A. HOADLEY *in the Chair.*

The following report was presented for final action:

No. 2522.—Gaede's Molecular Air-Pump. Elliott Cresson Medal. Adopted.

The following reports were presented for first reading:

No. 2527.—Norton "Alundum."

No. 2535.—Tirrill Voltage Regulator.

No. 2543.—Kinkead Shaft-Levelling Device.

R. B. OWENS,
Secretary.

SECTIONS.

A meeting of the Electrical Section was held in the Hall of the Institute on Thursday evening, October 2, 1913, at 8 o'clock.

Mr. W. C. L. Eglin, President, occupied the chair.

The minutes of the previous meeting were approved as published.

Dr. Chas. P. Steinmetz, Consulting Engineer, General Electric Company, and Professor of Electrical Engineering, Union College, Schenectady, N. Y., presented a paper entitled "The Effect of Electrical Engineering on Modern Industry."

The speaker considered the economy of the present methods of industrial production of electrical energy and outlined the adjustments of operating conditions necessary to increase this economy.

After some discussion, the thanks of the meeting were extended the speaker.

Adjourned.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

Elections to Membership.

(Stated Meeting of the Board of Managers, October 8, 1913.)

RESIDENT.

MR. FRANCIS X. DAILY, 1521 North Seventeenth Street, Philadelphia, Pa.

NON-RESIDENT.

MR. LUTHER D. BURLINGAME, 15 Catalpa Road, Providence, R. I.

MR. RALPH E. FLANDERS, Jones & Lamson Machine Company, Springfield, Vt.

MR. GEORGE A. ORROK, 232 East Seventeenth Street, Flatbush, N. Y.

MR. JOHN RIDDELL, General Electric Company, Schenectady, N. Y.

ASSOCIATE.

MR. JOHN MCALLISTER, Gibbsboro, N. J.

Changes of Address.

MR. W. S. ATKINSON, 90 Bartley Avenue, Mansfield, Ohio.

MR. HAROLD V. COES, 982 Beacon Street, Newton Centre, Mass.

MISS EMILY E. HOWSON, 222 Langdon Street, Madison, Wis.

PROF. G. LANZA, The Montevista, Sixty-third and Oxford Streets, Philadelphia, Pa.

MR. NORMAN MACBETH, 246 West End Avenue, New York City, N. Y.

MR. DONALD MCDONALD, Louisville Gas and Electric Company, 311 West Chestnut Street, Louisville, Ky.

MR. LOUIS M. PAWLETT, 771 Myrtle Avenue, Bridgeport, Conn.

LIEUT.-COL. SAMUEL REBER, Signal Office, War Department, Washington, D. C.

MR. FREDERICK W. SALMON, 719 Eighteenth Street, Birmingham, Ala.

MR. RICHARD SELLERS, Bellevue, Del.
MRS. WILLIAM SELLERS, Bellevue, Del.
MR. ELMER A. SPERRY, The Sperry Gyroscope Company, 126 Nassau Street, Brooklyn, N. Y.
MR. G. VON UTASSY, 119 West Fortieth Street, New York City.
MR. ROBERT W. WITHINGTON, The American Insulating Machine Company, corner Fairhill and Huntingdon Streets, Philadelphia, Pa.
MR. H. S. WORRELL, 36 East Montgomery Avenue, Philadelphia, Pa.

LIBRARY NOTES.

Purchases.

American Electrochemical Society Transactions, vol. 23. 1913.
COHN, G.—Die Pyrazolfarbstoffe. 1910.
COLVIN, F. H., and F. A. STANLEY.—American Machinist Grinding Book. 1912.
GREENE, A. M., JR.—The Elements of Heating and Ventilation, 1st edition. 1913.
HELDT, P. M.—The Gasoline Automobile, vol. 2. 1913.
International Geological Congress, XII, Canada.—The Coal Resources of the World. 4 vols. 1913.
LORD, N. W., and D. J. DEMOREST.—Metallurgical Analysis, 3d edition. 1913.
MARTIN, G.—Industrial and Manufacturing Chemistry Organic. 1913.
RYAN, W. T.—Design of Electrical Machinery. 3 volumes, 1st edition. 1912.
SCHULTZ, G.—Farbstofftabellen. 1911–1913.
SODDY, F.—The Interpretation of Radium. 3d edition. 1912.

Gifts.

American Institute of Metals, Transactions, vol. 6. Buffalo, 1913. (From the Institute.)
American Society for Testing Materials, Year-Book 1913. No place, 1913. (From the Society.)
Associations des Ingénieurs Sortis des Cinq Écoles Belges, Annuaire général des ingénieurs diplômés en Belgique, 2d edition, 1912. Gand, Belgium, no date. (From the Association.)
Baldwin Locomotive Works, Forty Thousandth Locomotive. Philadelphia, 1913. (From the Works.)
Baltimore Department of Health, Annual Report, 1912. Baltimore, 1912. (From the Department.)
Boston and Maine Railroad, 80th Annual Report, 1913. Boston, 1913. (From the Railroad.)
Canada Department of Mines: Economic Minerals and Mining Industries of Canada. Ottawa, 1913. (From the Department.)
Canada Department of Mines: Memoir 33, The Geology of Gowanda Mining Division, by W. H. Collins. Ottawa, 1913. (From the Department.)
Canadian Mining Institute, Index of the Journal, vols. 1–10, 1898–1907. Montreal, 1913. (From the Institute.)

Canadian Pacific Railway Company, Report of the 32d Annual Meeting. Montreal, 1913. (From the Company.)

Canadian Society of Civil Engineers, Transactions, vol. 26, part 2. Montreal, 1913. (From the Society.)

Chicago & North-Western Railway Company, 54th Annual Report, June 30, 1913. Chicago, 1913. (From Mr. R. D. Jenks.)

Chicago, Rock Island & Pacific Railway Company, 33d Annual Report, June 30, 1913. Chicago, 1913. (From the Company.)

Denver & Rio Grande Railroad Company, 27th Annual Report, 1913. No place, no date. (From the General Auditor.)

Detroit Twist Drill Company, Catalogue No. 16 and Form No. 18, Drills. Detroit, no date. (From the Company.)

Drexel Institute, Year-Book 1913–1914. Philadelphia, 1913. (From the Institute.)

Engineers' Club of Philadelphia, Directory 1913. Philadelphia, 1913. (From the Club.)

Gold Car Heating and Lighting Company, Catalogue 1910, Gold Systems of Heating and Lighting of Railway Cars. New York, no date. (From the Company.)

Great Britain Meteorological Committee, Eighth Annual Report, 1913. London, 1913. (From the Meteorological Department.)

Jefferson Physical Laboratory of Harvard University, Contributions, vol. 10, 1912. Cambridge, Mass., 1913. (From the Laboratory.)

K. Vitterhets Historie och Antikvitets Akademien, Fornvännen, 1912. Stockholm, Sweden, no date. (From the Akademien.)

Lake Mohonk Conference on International Arbitration, 19th Report, May, 1913. Mohonk Lake, 1913. (From the Secretary.)

Lewis Institute, Annual Register, 1912–1913. Chicago, 1913. (From the Institute.)

Maryland Geological Survey, Devonian, 3 volumes. Baltimore, 1913. (From the State Geologist.)

Mason Regulator Company, Catalogue No. 66, Pressure Regulating Devices. Boston, 1913. (From the Company.)

Massachusetts Board of Gas and Electric Light Commissioners' 28th Annual Report, 1912. Boston, 1913. (From the Board.)

Mellon Institute of Industrial Research and School of Specific Industries: Smoke Investigation Bulletin No. 4, The Economic Cost of the Smoke Nuisance to Pittsburgh, by John J. O'Connor, Jr. Pittsburgh, 1913. (From the Institute.)

Minneapolis, St. Paul & Sault Ste. Marie Railway Company, 25th Annual Report. Minneapolis, 1913. (From the Company.)

Minnesota Railroad and Warehouse Commission, 28th Annual Report, 1912. Minneapolis, 1913. (From the Commission.)

New South Wales Department of Mines: Mineral Resources No. 7, Mercury or Quicksilver in New South Wales, by J. E. Crane. Sydney, 1913. (From the Minister for Mines.)

Newton City Engineer, Annual Report, 1912. Newton, Mass., 1913. (From the City Engineer.)

New York, Ontario & Western Railway Company, 34th Annual Report. New York City, 1913. (From the Company.)

New York State Public Service Commission for the First District, Report for 1911, vol. 3. New York, no date. (From the Commission.)

New York State Public Service Commission for the Second District, Sixth Annual Report, 1912, 2 volumes. Albany, 1913. (From the Commission.)

Ohio Chief Inspector of Mines, 38th Annual Report, 1912. Springfield, 1913. (From the Inspector.)

Ohio Northern University, Catalogue 1913–1914 and Calendar 1913–1914 of the College of Engineering. Ada, 1913. (From the University.)

Ohio State University, Catalogue May, 1913. Columbus, 1913. (From the University.)

Ontario Bureau of Mines: Report vol. 19, part 2, The Cobalt-Nickel Arsenides and Silver Deposits of Temiskaming, by W. G. Miller. Toronto, 1913. (From the Bureau.)

Ontario Entomological Society, 43d Annual Report. Ontario Fruit Growers' Association, 44th Annual Report. Toronto, 1913. (From the Ontario Department of Agriculture.)

Osaka Imperial Mint, Report of the Director, 1913. Osaka, Japan, 1913. (From the Director.)

Patents, Copyrights and Trade-Marks, by W. Henry Elfreth. New York, 1913. (From the Author.)

Philadelphia Museums, Annual Report 1912. Philadelphia, 1913. (From the Museums.)

Philadelphia Transit Commissioner, Report July, 1913, vols. 1 and 2. Philadelphia, no date. (From the Director of the City Transit.)

The Railway Library, 1912, edited by Slason Thompson. Chicago, 1913. (From the Editor.)

Royal Society of Canada, Proceedings and Transactions, 3d series, vol. 6, 1913. Ottawa, 1913. (From the Honorable Secretary.)

St. Louis Water Commissioner, Annual Report April, 1913. St. Louis, 1913. (From the Commissioner.)

Staffordshire Iron and Steel Institute, Proceedings, vol. 28, 1912–1913. Stourbridge, England, 1913. (From the Institute.)

L. S. Starrett Company, Catalogue No. 20, Fine Mechanical Tools. Athol, Mass., no date. (From the Company.)

Statistisches Taschenbuch für das Deutsche Reich. von Erich Simon, 4th Jahrgang, 1913. Berlin, 1913. (From Mr. R. D. Jenks.)

Tasmania Department of Mines: Geological Survey Bulletin No. 13, The Preolenna Coal Field and the Geology of the Wynyard District, by Loftus Hills. Hobart, 1913. (From the Department.)

Tasmania Secretary for Mines, Report 1912. Hobart, 1913. (From the Secretary.)

Technische Hochschule zu Karlsruhe, 25 publications issued during the school year 1912–1913. Karlsruhe, Germany, 1912–1913. (From the Hochschule.)

Triumph Ice Machine Company, Catalogue E, Triumph Ammonia Fittings. Cincinnati, 1913. (From the Company.)

University of Pennsylvania, Catalogue 1912–1913. Philadelphia, 1913. (From the University.)

Victoria Mines Department, Annual Report of the Secretary for Mines, 1912. Melbourne, 1913. (From the Secretary.)

Western Australia Statistical Register, 1911. Perth, 1913. (From the Registrar General.)

Wisconsin Geological and Natural History Survey Bulletin No. 26, The Geography and Industries of Wisconsin, by Ray Hughes Whitbeck. Madison, 1913. (From the Survey.)

Wisconsin State Historical Society, Collections, vol. 20. Madison, 1911. (From the Society.)

Henry R. Worthington Pump Company, "Irrigation": Conservation and Distribution of Water for Irrigation. New York, no date. (From the Company.)

Yale University, Report of the Treasurer, 1912–1913. New Haven, 1913. (From the University.)

BOOK NOTICES.

U. S. DEPARTMENT OF AGRICULTURE.—Bureau of Plant Industry, Bulletin No 285: "The Water Requirement of Plants," a review of the literature, by Lyman J. Briggs, Biophysicist in Charge of Biophysical Investigations, and H. L. Shantz, Plant Physiologist. 96 pages, illustrations, 8vo. Washington, Government Printing Office, 1913.

This review of the literature on the water requirement of plants supplies an extended bibliography of the subject and presents the results of the leading experiments.

Among the topics considered are the effect of soil moisture content, soil type, cultivation, soil mass, fertilizers, previous crops, soil temperatures, air temperatures, shade, air, humidity, carbon dioxide content of the air, parasites, the relative leaf area, frequent cutting, defoliation, amount of growth or number of plants per unit of soil mass, and the bearing of the age of the plant on its water requirement.

In addition, there is a consideration of the water requirement of different kinds of plants, and the determination of water requirement of crops under field conditions.

JOURNAL OF AGRICULTURAL RESEARCH.—The first number of the new *Journal of Agricultural Research* published by the U. S. Department of Agriculture was issued October 10th. It consists of eighty-seven pages of letter-press and line drawings and five plates, including one color plate. The articles in the first number are:

Citrus Ichangensis, a Promising, Hardy, New Species from Southwestern China and Assam.

Cysticercus Ovis, the Cause of Tapeworm Cysts in Mutton.

The Serpentine Leaf-Miner.

The introduction is written by Dr. B. T. Galloway, Assistant Secretary, and outlines the purposes of the journal.

The first few issues will contain papers from the Department of Agriculture only. The later numbers, however, will probably include articles prepared and submitted by investigators in the State agricultural colleges and experiment stations. The book is highly technical in character and will not be circulated except among scientific specialists.

PUBLICATIONS RECEIVED.

Electrical and Magnetic Calculations for the Use of Electrical Engineers and Artisans, Teachers, Students and all others Interested in the Theory and Application of Electricity and Magnetism, by A. A. Atkinson, M.S., Professor of Physics and Electrical Engineering in Ohio University, Athens, Ohio. Fourth edition. 310 pages, illustrations, plates, 12mo. New York, D. Van Nostrand Company, 1913. Price, $1.50.

Physical Measurements, by A. Wilmer Duff, Professor of Physics in the Worcester Polytechnic Institute, and Arthur W. Ewell, Professor of Physics in the Worcester Polytechnic Institute. Third edition, revised and enlarged. 244 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son & Co., 1913. Price, $1.50.

A New Era in Chemistry. Some of the Most Important Developments in General Chemistry during the last Quarter of a Century, by Harry C. Jones. 326 pages, 12mo. New York, D. Van Nostrand Company, 1913. Price, $2.

The Gyroscope, by F. J. B. Cordeiro. 105 pages, illustrations, 12mo. New York, Spon & Chamberlain, 1913. Price, $1.50.

Canada Department of Mines: Economic Minerals and Mining Industries of Canada, by the Staff of the Mines Branch. 77 pages, illustrations, map, 8vo. Ottawa, Government Printing Bureau, 1913.

Business Methods in Municipal Works. An Informal Record of the Operations of the Department of Public Works of the City of Philadelphia under the Administration of Mayor Blankenburg. 64 pages, 8vo. Philadelphia, Department of Public Works, 1913.

A Nation's Neglect, by Marcus A. Dow, General Safety Agent, New York Central Lines. Reprinted from the *Outlook,* issue of September 27, 1913. 10 pages, illustrations, 8vo. New York, Kempster Printing Company, 1913.

Diagram Giving Stresses in Beams, by H. R. Thayer, Assistant Professor of Structural Design, Carnegie Institute of Technology. Sheet 9 × 12 inches. New York, D. Van Nostrand Company, 1910. Price, 20 cents.

Seventh Annual Convention Illuminating Engineering Society, Souvenir Program. 40 pages, illustrations, 12mo. Pittsburgh, Pa., issued by General Convention Committee, 1913.

U. S. Bureau of Mines: Bulletin 22, Analyses of Coal in the United States, with description of mine and field samples collected between July 1, 1904, and June 30, 1910, by N. W. Lord, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford. Part I—Analyses; Part II—Descriptions of Samples. 2 volumes, 8vo. Bulletin 64, The Titaniferous Iron Ores in the United States: Their Composition and Economic Value, by Joseph T. Singewald, Jr. 145 pages, illustrations, plates, 8vo. Technical Paper 33, Sanitation at Mining Villages in the Birmingham District, Alabama, by Dwight

E. Woodbridge. 26 pages, illustrations, map, 8vo. Technical Paper 43, The Influence of Inert Gases on Inflammable Gaseous Mixtures, by J. K. Clement. 24 pages, illustrations, plates, 8vo. Monthly Statement of Coal-Mine Fatalities in the United States, July, 1913, with revised figures for preceding months, compiled by Albert H. Fay. 19 pages, 8vo. Washington, Government Printing Office, 1913.

The Cost to the United States and its Cotton Producers of the Clarke Amendment to the Tariff Act Imposing a Prohibitive Tax on Contracts for the Future Delivery of Cotton made upon Cotton Exchanges, by Arthur Richmond Marsh. 15 pages, 8vo. New York, 1913.

U. S. Department of Commerce and Labor: Circular of the Bureau of Standards, S. W. Stratton, Director. No. 42, Metallographic Testing. 16 pages, 8vo. Washington, Government Printing Office, 1913.

Mellon Institute of Industrial Research and School of Specific Industries: Smoke Investigation.—Bulletin No. 4, The Economic Cost of the Smoke Nuisance to Pittsburgh, by John J. O'Connor, Jr., A.B. 46 pages, 8vo. Pittsburgh, Pa., University of Pittsburgh, 1913.

Canada Department of Mines: A General Summary of the Mineral Production of Canada during the Calendar Year 1912, by John McLeish, B.A., Chief of the Division of Mineral Resources and Statistics. 46 pages, 8vo. Ottawa, Government Printing Bureau, 1913.

U. S. Department of Agriculture: Bulletin No. 12, Uses of Commercial Woods of the United States, by H. W. Maxwell, Expert. 54 pages, 8vo. Bulletin No. 23, Vitrified Brick as a Paving Material for Country Roads, by Vernon M. Peirce, Chief Engineer, and Charles H. Moorefield, Senior Highway Officer, Office of Public Roads. 34 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1913.

South Philadelphia: The Abolishment of Grade Crossings and the Creation of Opportunities for Commercial and Industrial Development. 72 pages, illustrations, plates, tables, 8vo. Philadelphia, Department of Public Works, 1913.

The Registration of Vital Statistics and Good Business, an address delivered before the Annual Conference of Health Officers of the State of Indiana, Indianapolis, May 13, 1913, by Louis I. Dublin, Ph.D., Statistician Metropolitan Life Insurance Company. 16 pages, illustrations, 8vo. New York, 1913.

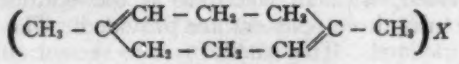
Ontario Bureau of Mines: Report vol. xix, part ii, The Cobalt-Nickel Arsenides and Silver Deposits of Temiskaming (cobalt and adjacent areas), by Willet G. Miller, Provincial Geologist. Fourth edition. 279 pages, illustrations, plates, maps, 8vo. Toronto, King's Printer, 1913.

Railway Routes in Alaska: Message from the President of the United States Transmitting Maps and Profiles to Accompany the Report of the Alaska Railroad Commission. 19 plates, maps, profiles, 8vo. Washington, Government Printing Office, 1913.

U. S. Department of Commerce: Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory near Honolulu, Hawaii, 1911 and 1912, by Daniel L. Hazard, Computer, Division of Terrestrial Magnetism. 99 pages, plates, quarto. Washington, Government Printing Office, 1913.

CURRENT TOPICS

Artificial Caoutchouc from the Scientific Aspect. C. HARRIES. (*Chem. Zeit.*, xxxvi, 654.)—Emphasis is laid on the ozone method of investigating the structure and composition of synthetic caoutchoucs. This method has proved the chemical identity of synthetic isoprene caoutchouc with the natural product. The ozonide of sodium-isoprene caoutchouc, on the other hand, gives a different scission curve and different decomposition products, therefore its chemical nature must be entirely different. The so-called piperylene caoutchouc, obtained by heating α-methylbutadiene, contrary to expectation, proved to be different from isoprene caoutchouc, while gutta-percha resembles it closely, though very different externally. The study of the ozonide has proved that the doubly unsaturated δ-ring lies at the basis of the normal rubbers, isoprene caoutchouc having the formula



is still unknown. In the case of butadiene caoutchouc, theory is proved by fact, because its ozonide is identical with that obtained from Willstaetter's 1.5-cyclo-octadiene and gives the same quantity of succinic dialdehyde on decomposition with water. This explains why rubber and gutta-percha give the same ozonide. They are both polymers of the same hydrocarbon, and the difference lies only in the molecular weight.

Dried Bagasse as Fuel. ANON. (*Engineering*, xciii, 727.)—One pound of undried bagasse with 53.5 per cent. water evaporates 1.63 pounds water, while with dried fuel, having 45.4 per cent. water, there is evaporated 2.53 pounds water from and at 100° C.

Tungsten Daylight Lamp. ANON. (*Electrical World*, lxi, 1181.)—In most artificial illuminants, including the tungsten lamp, there is an excess of the red end of the spectrum as compared with daylight. This is illustrated by a diagram. Siemens and Halske have introduced a special screen which, when used with a tungsten lamp, gives progressively increasing absorption in the spectrum between 0.48 μ and 0.62 μ. This gives a light approximating in color to daylight for practical purposes, although not exactly equivalent. The lamp is available for voltages from 100 to 130 and 200 to 250. The candle-power is from 70 to 75, and the specific consumption about 1.4 watts per candle-power.

Pinch Effect Electric Furnace. ANON. (*Eng.*, xcv, 2477, 848.)—Dr. Carl Hering, of Philadelphia, demonstrated his process at the Northampton Institute at a meeting of the Faraday Society. The furnace was a small model, and lead was the metal used. Dr. Hering stated that several large furnaces were under construction, one being a three-ton steel furnace. Explaining the principle of his pinch effect, Dr. Hering referred to his well-known type of T-shape furnace, consisting of a vertical tube which opens out at the top to a circular basin. The electrode—a block of steel or of the respective metal—forms the bottom of this tube; above it is the metal, which rises along the axis of the tube at such a speed that a sort of fountain of fused metal is produced. According to Dr. Hering, a jet of liquid metal, through which a very strong electric current is passed, is crushed by electro-magnetic forces, which tends to squeeze the metal out, or up in this case; others explain the effect by the mutual attraction of the parallel lines of force. Dr. Hering further assumes a force which tends to stretch the conductor. In any case the heat developed by intense currents in a restricted conductor is very high, a brisk circulation is set up, and impurities of the metal are carried up to the surface and stay there. As a rule, two parallel resisters or tubes are provided, with an electrode at the bottom of each; on three-phase circuits three resisters are provided. The tubes may be horizontal or inclined. The small furnace shown consisted of an iron pan, mounted in bricks; one half of the pan served as crucible, the other half was taken up by a cubical block of magnesite provided with two parallel horizontal bores, about half an inch in diameter. At the one side the passages ended in vertical openings in the magnesite, through which the electrodes and electrode leads were inserted, and led on the other side to the bath. It could be seen that the metal rushed through both the passages into the molten bath; the motion stopped at once when the current was cut off, and set in again immediately on re-establishing the circuit. The electrodes were joined to the secondary of a transformer, and in actual practice the transformer is made to tilt with the furnace, if that is desirable. Dr. Hering expressed no preference for horizontal or inclined resisters, but remarked that in tilting furnaces the inclination could be altered at will. The resisters suffered less from mechanical erosion than was generally assumed, and the passages could easily be repaired; rammed-down magnesite was mostly used. The furnaces might be provided with several crucibles joined in parallel. They were recommended for steel refining, melting alloys, annealing, and ore smelting. In the latter case a start was made with the metal (*e.g.*, zinc), and a charge of ore and flux was added at the top. As the furnace was quite unobstructed above, although it might be covered, it was convenient for working in rarefied or compressed atmospheres of oxidizing or reducing character. The sulphur of a bad iron had been reduced to 0.006 per cent. in one melt. A counter electromotive force was set up in the hot metal, which was an advantage, since it was all converted into heat.

Cumberland's Electrical Process for the Protection of Boilers. ANON. (*Eng.*, xcv, 2477, 849.)—This process has been introduced into the United States with the view of preventing corrosion in boilers. It consists of the use of one or more electrodes installed in the boiler, and connected to the positive terminal of a direct-current supply, the boiler being connected to the negative terminal, and the water forms the electrolyte. It is stated that only enough voltage is required to overcome the resistance through the water, and any counter electromotive force due to the difference of potential of the metals of the boiler. A report issued by the United States Navy Department states that some experiments were carried out on a small fire-tube boiler having brass tubes, with a steel shell, in which five polished steel plates were placed: One on the crown sheet, one across the top row of brass tubes, one across the tubes about the middle of the nest of tubes, one on the bottom of the shell-plate under the furnace, and one at the smoke-pipe end. The boiler was filled with water, steam was raised to 190 pounds pressure per square inch, which was kept up for five days, after which the boiler was examined. There were no signs of hydrogen gas, and the electrode placed in the boiler was found to be considerably corroded. The brass tubes showed no corrosion, nor was there corrosion on the test pieces. Underneath the cathode and on the tubes and shell a deposit of black iron dust was found, which was easily washed off. Old scale had also been cracked off the crown sheet and shell in places. The scale on the brass tubes also was cracked off in places and could be easily washed away. The iron electrode in the water was very badly corroded.

Illumination of Interiors. P. S. MILLAR. (*Amer. Illum. Engin. Soc. Trans.*, viii, 99.)—After some preliminary remarks on the objects of illuminating engineering, the author describes some experiments with small model interiors, each 4 feet long, 4 feet wide, and 3½ feet high. These were used to illustrate the effect of various forms of reflectors, direct and indirect lighting, correct and incorrect positions of lamps, etc. The absorption of various globes is given as follows: Frosted, 6 per cent.; light opal, 13 per cent.; dense opal, 22 per cent. The horizontal illumination with indirect light from ceilings of varied reflecting powers is stated to be (taking a white ceiling as 100): Light cream, 87 per cent.; dark cream, 58 per cent. The illumination derived from direct, semi-indirect, and indirect lighting, with a given expenditure of energy, was found to be: Direct, 1.61 candle-feet; semi-indirect, 1.33 candle-feet; indirect, 0.91 candle-feet.

Slow Ions in Liquid Dielectrics. H. J. VAN DER BIJL. (*Deutsch. Phys. Gesell. Verh.*, xv, 4, 102.)—A discussion on the formulæ for the motion of ions in very viscous media, with special reference to ions produced by radium rays and by ultra-violet light, in vaseline and in aniline.

Osmium-Platinum: a New Alloy. F. ZIMMERMANN. (*Brass World*, ix, 9, 314.)—Of the several metals of the platinum group, platinum, palladium, iridium, and rhodium have been generally used in the industrial arts, either alone or in combination as bivalent alloys. Iridium-platinum is the best known, but the increasing scarcity of iridium has led to the search for other combinations of the metals of this group, yielding alloys possessing physical and chemical properties of equal, if not greater, value. The rarer metals of the platinum group are not easily obtained in great purity, and for this reason but little success has been obtained when combined as bivalent alloys. The strong affinity of osmium for oxygen has increased the difficulty of alloying it with other metals in definite proportions. After many experiments the author has successfully combined highly-refined platinum and osmium in widely varying proportions, yielding alloys of commercial value. The two metals may be alloyed in almost any proportions, yet alloys containing from 1 to 10 per cent. osmium and 99 to 90 per cent. platinum are chiefly used. Great purity of the components is essential, as small percentages of other elements appear to be very detrimental to the properties of the resulting alloy. According to the chemical and physical behavior, it seems that one part of osmium in an alloy with platinum will take the place of two and one-half times its weight of iridium. The osmium-platinum alloy is very acid-resisting; and its electrical resistance is considerably higher than that of a similar iridium-platinum alloy. It possesses great hardness and tensile strength, and wires of the finest sizes are drawn with comparative ease.

Power Matters in Textile Mills. F. W. DEAN. (*Eng.*, xcv, 2477, 842.)—A paper read before the National Association of Cotton Manufacturers, Boston, Mass. The question is reviewed under its various aspects. Speaking generally, electricity has so many advantages that probably it will be universally resorted to for power in driving textile mills. It permitted a central steam plant to be used under all circumstances; this added to efficiency and led to minimum charges of all kinds, especially in an "overgrown" mill now having several steam plants. The prime movers in the near future would be steam-turbines operated by superheated steam at a relatively high pressure. He was a strong advocate of fire-tube boilers; they were more economical, more easily cleaned and safer than water-tube boilers. In regard to the purchase of power from outside central stations, he had investigated the point, and had invariably found that it was advantageous for mills to produce their own power rather than to purchase power from an outside source; this was still more particularly the case for mills where a considerable amount of steam was used, and especially where exhaust steam could be utilized for dyeing, starting, heating, etc.

Deterioration of Fire-brick. G. RIGG. (*J. Ind. Eng. Chem.*, v, 549.)—A discussion on the causes of the deterioration of fire-bricks during use, and the conclusion is reached that, other things being equal, the resistance to the action of corrosive slags and gases is greater the more compact and close-textured the brick is. "Spalling" of close-textured brick is due to the use of unsuitable clay, or poor workmanship, or both. It is possible to prepare close-textured fire-brick containing considerable amounts of coarse material, provided that sufficient care be taken in sizing the "grog," so that the interstices between the larger fragments shall be filled as completely as possible by smaller fragments.

Protection of Iron Pipe. ANON. (*Amer. Mach.*, xxxix, 4, 142.)—Iron pipe can be protected from corrosion by heating in a muffle to 1000° F. and admitting steam at the same temperature. This forms a layer of magnetic iron oxide. Smith's process, however, gives better protection. The well-cleaned pipe heated to 700° F. is dipped into a mixture of pitch, coal-tar, and a little linseed oil, which is heated to 300° F. After a few minutes the pipe is drained vertically and cooled. The rapid oxidation of the linseed oil forms a tough binder, as in paint drying.

Absorption of Gas by the Electrodes in the Neon Tube. G. CLAUDE. (*Comptes Rendus*, clvi, 1317.)—It has been noticed that the electrodes in the neon tube do not readily absorb the gas. It has been found that if the tube is filled with a mixture of one per cent. helium in neon the helium gradually disappears; nitrogen is also absorbed much more readily than neon. In general, the spectrum of a tube containing other gases as impurities gradually changes, until only the neon spectrum remains. This characteristic is fortunate, as it means that a badly-filled tube tends to improve in use.

Utah Metal Production. ANON. (*Met. and Chem. Eng.*, xi, 8, 438.)—According to the U. S. Geological Survey, the total value of gold, silver, copper, lead, and zinc produced in Utah in 1912 was $42,922,302. There was a decrease of 10 per cent. in the value of gold produced compared with 1911; an increase of 10 per cent. in quantity of silver; a decrease in copper; an increase in lead, and about the same production in zinc. The total production showed an increase in value of about $6,000,000.

American Agricultural Machinery. ANON. (*Eng.*, xcv, 2477, 857.)—The exports of agricultural machinery from the United States in 1911 reached a value of $36,241,000. This total was made up as follows: To Russia, $14,164,000; Argentina, $13,692,000; Canada, $8,284,000; Germany, $4,046,000; Austria-Hungary, $3,400,000; Australia, $2,945,000; and Great Britain, $2,687,000.

Interference Phenomena with Röntgen Rays. W. FRIEDRICH, P. KNIPPING, and M. LAUE. (*K. Bayer. Akad. München. Ber.*, 303.)—According to the generally-accepted theory, the atoms in crystals are arranged in a regular manner as regards spacing throughout the whole crystal. Therefore, if X-rays fall on a crystal, interference effects ought to be observed if the X-rays are similar to light-waves of very short wave-length. In the experiments described a narrow pencil of X-rays fell on a crystal having a photographic plate placed behind it and normal to the beam. Exposures of many hours were made, and on development it was found that, in addition to the central image caused by the main beam, regularly-arranged spots were present on the plate. With powdered copper-sulphate, for example, no such effects were observed. The effects were found with crystals of copper sulphate, rock-salt, diamond, and zinc blende. With the plate of the latter (a cubic crystal) $1.0 \times 1.0 \times 0.05$ cm., cut parallel to one of its principal axes, an extended series of photographs was made with the crystal orientated at different angles. A theoretical examination of the position of the spots in the various photographs is given by M. Laue, the crystal being treated as a three dimensional diffraction grating and the spots as due to the reinforcement of the waves in different directions. The calculated positions of the spots are in good agreement with theory, it being also assumed that definite wave-lengths are present, presumably corresponding to the characteristic X-radiations from the zinc and the sulphur. Five definite wave-lengths are given, varying between 1.27 and 4.83×10^{-9} cm.

The Corrosion of Bronze Propellers. W. RAMSAY. (*Engineering*, xciii, 687.)—The remarkable corrosion of bronze propeller blades used with steam turbines is probably the result of electrolytic action. That part of the blade which is exposed to great strain becomes the anode, while the normal part becomes the cathode, and in the salt water, as an electrolyte, a current flows between them. The hardened or strained metal is attacked or dissolved, while the unstrained metal is comparatively unaffected. The weight of the propeller blades has been reduced too much, they should be stiffened enough to prevent flexure.

The "Oriona" Lamp. DE KERMOND. (*Électricien*, xlv, 357.)—This form of lamp consists of a series of tungsten filaments mounted in a horizontal plane in order to improve the illumination immediately under the lamp. It is also possible to make the same arrangement in a vertical plane, or to use a combination of the two methods, so as to obtain the particular distribution of light that circumstances demand. Polar curves contrasting the distribution of light with that from an ordinary tungsten lamp are given. It appears there is an actual gain in the total light emitted, as well as an improvement in the lower hemisphere.

Effect of Foreign Metals on the Rolling of Zinc. E. PROST and A. VAN DE CASTEELE. (*Bull. Soc. Chim. Belg.*, xxvii, 175.)—Ingots weighing 40 pounds were prepared by casting together zinc alloys of various metals, with spelter containing lead 1.05 to 1.25, cadmium 0.076 to 0.11, and iron 0.03 to 0.039 per cent. The conclusions are: *Cadmium* is harmful above 0.25 per cent.; with 0.5 per cent. rolling is impossible. *Arsenic:* 0.02 per cent. markedly increases the hardness, and with 0.03 per cent. the metal is too brittle for practical purposes. *Antimony* is less objectionable than arsenic as regards hardness, as 0.07 per cent. does not increase the hardness; but 0.02 per cent. is enough to produce a striated surface on the rolled sheet, which makes it unsalable. *Tin* is objectionable when above 0.01, and prohibitive at 0.03 per cent. *Copper* has no hardening effect until it reaches 0.08, and with 0.19 per cent. the zinc is unworkable. *Iron:* 0.12 per cent. is a permissible maximum, but this is easily reduced in refining. *Lead:* Though 1 to 1.25 per cent. does not interfere with the rolling, a slight increase not only seriously affects malleability, but the excess of lead remains unalloyed and forms patches on the sheet. The presence of two or more impurities together results in a combination of the injurious effects of each.

Copals from Mozambique. ANON. (*Bull. Imp. Inst.*, xi, 221.)—The results of the examination of nine samples of "recent" copals (*i.e.*, from existing trees) are given. Most of the samples were of poor quality and too soft to produce satisfactory varnishes, but the "Mgeji" copal from trees growing in the Madanda forest was of good quality. Four grades of this copal were supplied and they were valued at about $25.00, $21.00, $12.50, and $6.25 respectively. They were not completely soluble in alcohol, ether, chloroform, benzene, or oil of turpentine; practically insoluble in a mixture of benzene and oil of turpentine, but partially soluble in mixtures of alcohol and ether, alcohol and benzene, and alcohol and oil of turpentine. They all became soluble in oil of turpentine on "melting" for 1½ hours, and in this process lost 14, 16, 21, and 30 per cent. respectively in weight. Varnishes prepared by dissolving the melted copals in oil of turpentine gave almost colorless, hard and glossy coatings in the case of the two more valuable grades, and pale yellowish-brown coatings in the case of the other two.

Variable-speed Aëroplanes. G. DE SAINT-AUBIN. (*Comptes Rendus*, clvi, 1131.)—This suggests the use of auxiliary planes carried on each side of the ordinary planes, and pivoted on horizontal axes passing through the centres of pressure. These auxiliary planes would be free on these axes when flying at high speeds, and thus would not have any supporting action. On descending, or when at low speeds, they would be controlled and act as extensions of the main planes.

Applications of Calcium. ANON. (*Brass World,* ix, 9, 317.)—From *The Ironmonger:* At the recent Foundry Exhibition at Leipzig a display of metallic calcium, as used for improving and purifying molten metals, was exhibited by the Bitterfeld Electro-Chemical Works. Metallic calcium, produced by an electrolytic process from molten calcium chloride, is industrially applied as an energetic purifying agent. It combines with oxygen, nitrogen, and hydrogen with rise of temperature; this increases the temperature of the molten bath and causes vigorous ebullition, whereby the gases, oxides, and portions of slag, dissolved or mixed with the bath, are brought to the surface. This complete purification produces a denser casting with a homogeneous texture. As calcium does not alloy with iron, but always goes into the slag, an excessive addition does not become injurious, as is the case with aluminum and other purifiers. Aluminum readily alloys with iron and causes an abundant separation of graphite which makes the iron pasty. Calcium promotes a thorough mixing and uniformity of the molten bath, thus permitting the use of iron which cannot generally be employed without danger to the good qualities of the product. For the complete deoxidation and refining of a normal melting, an addition of about 50 grammes of calcium per 100 kilogrammes is required. Calcium is also generally recommended for use in the founding of copper and other metals, but then the addition of calcium should not exceed 0.05 per cent. Metallic calcium is sold in airtight tin boxes, as it readily oxidizes on exposure to the air.

The Affinity of Cotton for Dyes. C. FAVRE. (*Bull. Soc. Ind. Mülhouse,* lxxxii, 183.)—In printing, and particularly in dyeing, the affinity of cotton for dyes is appreciably diminished by high temperature. This diminution is greater the higher the temperature and the longer the treatment. Steaming under pressure decreases the affinity of cotton for dyes more than high temperature. Mercerized cotton is more affected than ordinary cotton. If the cotton is moist, several hours of steaming under pressure produces only a slight difference in shade. Mordanting with glycerol or glucose protects the cotton, so that light and dark shades can be produced by printing with glycerol, steaming five minutes under 1 kilogramme pressure and then dyeing. Can-drying also weakens the affinity of cotton for dyes.

Absorption of Light by Half-frosted Lamps. A. J. MAKOWER and U. A. OSCHWALD. (*Electrician,* lxxi, 96.)—Comparisons of the distribution of light from bare and half-frosted lamps of various makes are described. The amount of light absorbed in the lower hemisphere varies according to the structure of the filament, being different in the case of carbon and metal filament lamps; there are considerable variations in the results obtained with different makes of carbon filament lamps. In general, half-frosting reduces the mean hemispherical candle-power by about 10 to 20 per cent.

Manganese-Bronze Castings for Valves. ANON. (*Brass World,* ix, 9, 315.)—Although manganese-bronze is much stronger than ordinary tin bronze, it is unsuitable for valves or other castings required to stand pressure, on account of the dross in the casting. Manganese-bronze cannot be cast without aluminum, the presence of which is *absolutely* essential for a successful casting. When aluminum, or any alloy containing it, is melted it oxidizes, and the oxide forms dross, through which leakage occurs when pressure is applied. The making of good castings depends upon: (1) The metal must be poured at as low a heat as possible, or at a temperature at which no smoke is given off from the undisturbed surface. If the metal is poured at so high a temperature that it smokes freely, the castings will be full of dross. However, care must be taken that the temperature is not so low that the metal is pasty when poured. (2) The metal must be cast "quietly," without any unnecessary agitation, to avoid exposing new surfaces to the air and causing oxidation which means dross. (3) The gating of the pattern and length of runner are very important. The runner should be as long as possible, so that what dross is in the metal when it enters the mould will remain in it. The use of the horn sprue will insure the best possible castings, as free from dross as possible. (4) Keep the sand as dry as possible, so there will be no bubbling or agitation of the metal when it enters the mould, as when manganese-bronze is agitated dross results. As a matter of economy the manufacture of manganese-bronze castings to stand pressure should not be attempted, but if unavoidable the casting will have to be done and the best made of a "bad job."

Instantaneous Braun-tube Photographs. J. ZENNECK. (*Phys. Zeitschr.,* xiv, 226.)—It has lately become possible to take instantaneous photographs of oscillographic curves by means of Braun's kathode-ray tube, owing to the increased luminosity available. The author describes an attachment to an ordinary camera suitable for taking such photographs, and reproduces some fine specimens of results, including that obtained with a damped condenser circuit of frequency 250 per second. The fluorescent substance used was Giesel's zinc sulphide.

New Alloy. ANON. (*Met. and Chem. Eng.,* xi, 8, 438.)—A new alloy, consisting of manganese, titanium, and silicon, has been patented by F. M. Becket, of Niagara Falls, N. Y. It may also contain carbon in proportions varying from a fraction of one per cent. to sufficient quantity to furnish all or part of the carbon required in the re-carburization of steel. The manganese and titanium together are preferably in excess of 50 per cent. of the alloy. When added to steel the component metals of the alloy are stated to diffuse through the molten mass more uniformly and rapidly than do the corresponding ferro-alloys.

Iron Moulds for Casting Brass. ANON. (*Brass World*, ix, 9, 305.)—Iron moulds are used in the brass industry, both in the rolling mill and brass foundry. In the rolling mill they are used for casting the brass into plates, rods, bars, billets, and tube-shells which are afterward rolled into sheet, rod, wire, and tubing. In the brass foundry they are used for making ingots. Cast iron is the only available metal for these moulds; semi-steel, malleable iron, and steel castings have all been tried, but all fail to give the service and all are more expensive. Any kind of cast iron will not answer for these moulds. For a *good* mould, the essentials are: (1) The mould must be composed of the right kind of iron,—*i.e.*, of a special, soft iron. (2) The mould must have a good surface. (3) The mould must be straight and flat.

If the iron is not soft, the mould will crack, sooner or later. A soft iron stands the heat better and lasts a long time; such an iron is high in silicon and low in combined carbon. The surface of the mould should be smooth and free from flaws or adhering sand. It need not be polished, and a good, smooth casting is satisfactory. Pickling in hydrofluoric acid is frequently resorted to in order to remove sand, and sand-blasting is good when necessary.

Micarta. ANON. (*Amer. Mach.*, xxxix, 3, 122.)—The Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pa., has developed a new material, known as micarta, as a substitute for hard fibre, glass, porcelain, hard rubber, built-up mica, pressboard, raw-hide, moulded compounds, etc. It is used for commutator bushings and brush holder insulation, noiseless gear blanks, conduit for automobile wiring, etc. It is a tan-brown, hard, homogeneous material having a mechanical strength about 50 per cent. greater than hard fibre. It can be sawed, milled, turned, tapped, and threaded, if a sharp-pointed tool is used and the work is done on a lathe. It can be punched in thin sheets only and cannot be moulded. Micarta is not brittle and will not warp, expand, or shrink with age or exposure to the weather; it takes a high polish, presenting a finished appearance. Two grades are made; the one known as "Bakelite micarta" will stand a temperature of 300° F. continuously, or 500° F. for a short time. It is infusible and remains unaffected by heat until a temperature sufficient to carbonize it is reached. It is impervious to moisture and insoluble in practically all of the ordinary solvents. The other grade, known as "No. 53 micarta," has the same mechanical and electrical properties as the "Bakelite micarta," but differs in its chemical and thermal properties.

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